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JOURNAL OF THE INSTITUTION OF PETROLEUM TECHNOLOGISTS

FOUNDED 1913——INCORPORATED 1914

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NOTICES.

The Institution as a body is not responsible for the statements of opinion expressed in any of its publications.

Copyright.—Publication of abstracts of Papers and articles appearing in the Journal is permitted, provided that acknowledgment is made to the Institution of Petroleum Technologists.

Papers and Articles.—The Council invites Papers and Articles both for reading at Ordinary Meetings of the Institution and for publication in the Journal. All Papers, whether for reading or publication, will be submitted to a referee appointed by the Publication Committee.

The Institution has published a brochure "Instructions for the Guidance of Authors" containing details of recommended practice in the preparation of Papers for publication. Copies of this brochure will be supplied on request.

Pre-Prints.—Advance proofs of Papers to be read at Ordinary Meetings are generally available about a week before the Meeting. Members wishing to be supplied with these pre-prints are requested to notify the Secretary.

Abstracts.—Members and Journal Subscribers desirous of receiving the Abstracts printed on one side of the paper only, can be supplied with these at a charge of 10*s.* per annum per copy, payable in advance.

Issue of Journal.—Members whose subscription is not in arrear receive the Journal free of cost. A member whose subscription is not paid by March 31st of the year for which it is due is considered to be in arrear.

Changes of Address.—Members are requested to notify any change of address to the Secretary.

Benevolent Fund.—The Benevolent Fund is intended to aid necessitous persons who are or have been members of the Institution, and their dependent relatives.

The Fund is raised by voluntary annual subscriptions, donations, and bequests, and all contributions should be sent to the Secretary of the Institution at Aldine House, Bedford Street, London, W.C. 2. The Fund is administered by the Council through the Benevolent Fund Committee, and all applications in connection therewith must be made on a special form which can be obtained from the Secretary of the Institution.

Appointments Register.—A register of members requiring appointments is kept at the offices of the Institution, and every effort is made to assist members of the Institution in search of employment.

Members who desire their names and qualifications to be included in this register are requested to apply to the Secretary for the Form of Application for Registration, if they have not already done so. Members residing in the London area are asked, if possible, to return this Form in person and make themselves known, together with their requirements, to the Secretary. It is also requested that members should notify the Secretary immediately they have obtained an appointment.

In submitting names of candidates to prospective employers it is understood that the Institution accepts no responsibility and gives no guarantee.

Library.—The Institution's Library may be consulted between the hours of 10 a.m. and 5.30 p.m. daily. (Saturdays, 10 a.m. to 12 noon.)

GENERAL MEETINGS.

General Meetings of the Institution will be held on the second Tuesday in each month at 5.30 p.m. at the Royal Society of Arts, John Street, Adelphi, London, W.C. 2.

Tea, coffee and light refreshments will be provided at 5 p.m. prior to each meeting.

Members may introduce visitors.

April 9th. **"The Boundary Friction of Oxidised Lubricating Oils."**
Dr. E. R. Redgrove, Ph.D., B.Sc., M.Inst.P.T.

May 14th. **"Drilling Muds."**
P. Evans, F.G.S., A.M.Inst.P.T., and A. Reid, A.M.Inst.P.T.

SUMMER MEETING AND ANNUAL DINNER.

A Summer Meeting of the Institution will be held in London on Friday, 28th June, 1935. Further details of this meeting will be announced in a subsequent issue of the *Journal*, but it is proposed to devote two sessions to the discussion of the Annual Reports on the Progress of Naphthology.

The Annual Dinner will be held at the Park Lane Hotel on the evening of Friday, 28th June.

INFORMAL DINNERS.

An informal Dinner is held at Gatti's Restaurant, King William Street, Strand, W.C. 2, immediately following each General Meeting of the Institution, to entertain the authors of Papers.

A cordial invitation is extended to all Members of the Institution.

The cost of the Dinner is 5*s.* (exclusive of wines). No separate notification of these Dinners will be issued.

STUDENTS SECTION.

(London Branch.)

Meetings of the Students Section (London Branch), unless otherwise notified, will be held at the Institution offices at 6.15 p.m. on the dates specified below.

Mar. 22nd. **"Health Hazards in the Petroleum Industry."**
J. McConnell Sanders, F.I.C., F.C.S. (Vice-President).

May 7th. **"Crooked Holes."**
A. J. Haworth (Student).

May 21st. To be announced later.

Tea and light refreshments will be provided at 5.30 p.m. prior to each meeting.

The Committee of the Students Section extends a cordial welcome to all Members of the Institution to attend the meetings of this Section.

NEW MEMBERS.

The following have been elected or transferred, subject to confirmation in accordance with By-Laws, Sect. IV, paras. 14–15, since the last issue of the *Journal*.

Members.

Bihoreau, Charles	Paris.
Frischknecht, Dr. Gustav	Trinidad.
Knighton, Charles William	London.
Melvill, Francis Leopold	Trinidad.

Associate Members.

Ananthanarayanan, K. S.	Singapore.
Booth, Donald Bartleman	Cockfosters.
Gray, George Edward	Hull.
Wasselin, Pierre Charles	L'Avera, France.

Transfer to Associate Members.

Froulkes-Jones, Rogers Garson	Trinidad.
Kelly, Michael Everitt	Abadan.

Student.

Mendell, Wilbert Thornton	London.

NOMINATIONS FOR MEMBERSHIP.

The following nominations for membership of the Institution of Petroleum Technologists were approved by the Council on 12th March, 1935, and the application forms may be seen at the offices of the Institution.

The names of the Proposer and Seconder are given in parentheses.

As Members.

Mardall, Evelyn George Campbell, Engineer, Trinidad Leaseholds, Ltd., Pointe-a-Pierre, Trinidad, B.W.I. (B. G. Banks; C. Capito.)

Voogt, George, Plant Manager, Shell-Works, Görnestr. 6, Hamburg 20, Germany. (I. J. F. Reydon; H. van der Waerden.)

Weymarn, Paul von, Geologist, 57, Yacob Aalls gate, Oslo, Norway. (A. Beeby Thompson; James Romanes.)

Whitney, James Gillis, Engineer, 76, Wood End Avenue, South Harrow, Middlesex. (Harold Moore; R. B. Hobson.)

As Transfer to Member.

Tett, Hugh Charles, Assistant Manager, Technical Dept., Anglo-American Oil Co., Ltd., 36, Queen Anne's Gate, S.W. 1. (D. S. Paul; E. B. Evans.)

As Associate Members.

Clark, Joseph, Fields Stores Assistant, c/o Burmah Oil Co., Ltd., Yenangyaung, Upper Burma. (G. W. Lepper; C. A. Sansom.)

Keplinger, C. H., Oil Production Engineer, 1140, South Gary Place, Tulso, Okla, U.S.A. (C. K. Francis; J. T. Hayward.)

WEATHERILL, Fred, Director, Heseltine Evelyn & Co., Ltd., 172, Buckingham Palace Road, S.W. 1. (D. S. Paul; H. C. Tett.)

WEBB, Terence Augustus, Refinery Foreman, c/o The Assam Oil Co., Ltd., Digboi, Assam, India. (P. Evans; F. A. Marr.)

WIGLEY, Ernest Robert John, Engineer, 16, Onslow Road, Rochester, Kent. (T. Cohn; F. W. S. King.)

As Transfer to Associate Member.

FRASER, Norman Colin, Engineer, 71, King's Road, Westcliff-on-Sea, Essex. (L. McG. Fraser; T. C. Palmer.)

As Associate.

MERRYWEATHER, Herbert Sydney, Chief Clerk, c/o Arend Petroleum Maatschappij, Aruba, N.W.I. (R. M. Beesley; R. C. Hales.)

BACK NUMBERS OF JOURNAL.

The Institution is desirous of purchasing a limited number of clean copies of Journal No. 19, April 1919, and No. 66, February 1928.

The price which will be paid for such copies is 7*s.* 6*d.*, and all inquiries should be sent to the Secretary.

STUDENTS SECTION.

The Committee of the Graduate Section of Institution of Automobile Engineers have extended an invitation to the Students of this Institution to attend their Annual Supper Dance, which is to be held at the Small Queen's Hall, Langham Place, W. 1, on Saturday, March 30th.

The price of a double ticket is 6*s.* and single ticket 3*s.* 6*d.*

Applications for tickets should be made to Mr. B. C. Ferguson, Hon. Secretary, Students Section (London Branch), St. Helen's Court, Great St. Helens, E.C. 3.

REPORT OF BALLOT FOR COUNCIL.

Six nominations were received to fill five vacancies on the Council.

The result of the Ballot, which was opened on March 12th and announced at the Annual General Meeting, was that the following were elected Members of the Council :

A. FRANK DABELL, M.I.Mech.E.
T. R. H. GARRETT, M.A., F.G.S.
Prof. V. C. ILLING, M.A., M.Inst.M.M.
E. R. REDGROVE, Ph.D., B.Sc., F.C.S.
CECIL W. WOOD, F.I.C.

PRESENTATION TO MR. A. FRANK DABELL.

The members of the Trinidad Branch of the Institution of Petroleum Technologists have presented an electric clock with walnut case, suitably inscribed, to Mr. A. Frank Dabell in appreciation of his services to the Branch since its inception in 1928.

The presentation was made on behalf of the Trinidad Branch by the President (Mr. T. Dewhurst) on the occasion of the Annual General Meeting on Tuesday, 12th March.

Mr. A. Frank Dabell was Chairman of the Trinidad Branch for the first five years of its existence, and served continuously on the Committee until his return to England in 1934. It was very largely due to Mr. Dabell's efforts that the Trinidad Branch was established on such a sound basis and that it has continued to prosper since its inception.

PERSONAL NOTES OF MEMBERS AND SPECIAL NOTICES.

It is suggested that members send information regarding their movements to the Secretary, for insertion under this heading.

Mr. A. E. Allen has left Egypt, and is now in Palestine.
Mr. C. Dales is returning home from Trinidad.
Mr. C. W. Fulcher is in Holland.
Mr. J. J. L. Hamilton is home from Japan.
Mr. J. Henry is now in Peru.
Mr. C. J. Johnson is home from Persia.
Mr. G. W. Lepper is on his way home from Burma.
Mr. G. H. May has left for Argentina.
Mr. S. R. Prisk is home from Burma.
Mr. C. S. Snodgrass has returned from the U.S.A.
Mr. T. Speight is now in Burma.

We are pleased to announce that the President of Venezuela has conferred upon Mr. F. G. Rappoport the Order of " El Libertador " in the Class of Officer.

The Secretary would be glad to learn of the addresses of the following members : J. M. Brown, A. F. H. Gee, M. Jawad Jafar, J. Cecil Jones, E. L. Leites, P. B. M. Linton, A. MacLean, B. F. N. Macrorie, W. J. Reynolds, W. McKecknie Robson, K. A. Spearing, and J. Towers.

ARTHUR W. EASTLAKE.
Honorary Secretary.

OBITUARY.

Dr. David White.

It is with deep regret that we record the death of Dr. David White, which occurred at his home in Washington, D.C., on 7th February, 1935.

Born in Palmyra, New York, on 1st July, 1862, he graduated from Cornell University in 1886 with the degree of Bachelor of Science. In the same year he entered the United States Geological Survey, serving as Chief Geologist from 16th November, 1912, to 16th November, 1922, and he was still with that organisation at the time of his death. His entire scientific career has therefore been linked with the Geological Survey, and his leadership and inspiring influence have affected and shaped its investigations.

During his service with the Survey he initiated numerous studies concerning the geology, development, and conservation of petroleum. These included the examination of underground temperatures, the relations of water, oil, and gas in rocks, the oil-shale resources of the U.S.A., the estimation of the petroleum reserves of the U.S.A.

Although Dr. White's researches in petroleum were extensive and far-reaching, they were only incidental to his life-time studies of fossil plants. His best known contribution, pertaining to the regional distribution of oil, is known as the carbon-ratio theory, and was based on his studies in the Appalachian and Mid-Continent areas. Here he discovered a significant relationship between the coals and the oil and gas deposits, which he stated as :—

" In regions where the progressive devolatilisation of the organic deposits in any formation has passed a certain point, marked in most provinces by 65 to 70 per cent. of fixed carbon (pure coal basis) in the associated or overlying coals, commercial oil pools are not present in that formation nor in any other formations normally underlying it, though commercial gas pools may occur in a border zone of higher carbonisation. The approximate carbonisation limits of the rocks containing or overlying oil pools may be found to vary somewhat in different provinces according to the characters of the original organic debris, the circumstances attending its deposition, and the geologic structure.

" Wherever the regional alteration of the carbonaceous residues passes the point marked by 65 per cent. or perhaps 70 per cent. of fixed carbon in the (pure) coals, the light distillates appear, in general, to be gases at rock temperatures. Occluded oils may, in some cases, have escaped volatilisation."

In recognition of his service in this field he received in 1931 from the National Academy of Sciences the Mary Clark Thompson gold medal for distinguished service in palæontology, and he was elected to honorary membership in the Geological Society of Belgium, and more recently in the Geological Society of China. He received the honorary degree of Doctor of Science in 1924 from the Universities of Cincinnati and Rochester and in 1925 from Williams College. He was a past-President of the Geological Society of America, a past Vice-President of the National Academy of Sciences and served for many years as its Home Secretary. For three

years he served as Chairman of the Division of Geology and Geography of the National Research Council, during which time he was primarily responsible for the initiation of important researches in petroleum. On account of his distinguished services in the field of economic geology he was awarded in 1931 the Penrose medal by the Society of Economic Geologists, and sixteen years ago he was elected to Honorary Membership in the American Association of Petroleum Geologists.

In 1934 he was awarded the Redwood Medal of the Institution of Petroleum Technologists. Dr. White was unable to receive the medal in person, but it was accepted on his behalf by the First Secretary of the American Embassy on the occasion of the Institution's Annual Dinner in June 1934.

To Mrs. White and members of the family we extend our very sincere sympathy in their bereavement.

Arnold Philip.

Mr. Arnold Philip, the late Admiralty Chemist, and for many years a prominent member of the Institution, died on February 16th at his residence, Upper Norwood, in his seventy-fifth year. Mr. Philip received his scientific training at the Royal School of Mines, and after graduating at London University was, for some time, Chemist at the Indian Engineering College, Cooper's Hill, and subsequently on the professorial staff at the Heriot Watt College, Edinburgh, and later on that of the Merchant Venturer's College, Bristol. He joined the Admiralty Service in 1902, and was appointed Admiralty Chemist in 1904, which post he held until his retirement in 1926.

His period of office in the Admiralty saw the gradual introduction of oil fuel into the Navy, and much of Mr. Philip's work was concerned with problems connected with petroleum and its products, on which subject he was regarded as an eminent authority.

Mr. Philip's scientific work covered a very wide field, and he was the author of many contributions to scientific and technical journals, notably on "Corrosion of Metals" and "Methods of Analysis of Oils." He was an active member of the Institution from its inception, and rendered very valuable assistance on the Standardization Committee.

F. G. Edmed.

STUDENTS SECTION—LONDON BRANCH.

SYNOPSES OF PAPERS, ETC.; JANUARY–MARCH, 1935.

An interesting programme of meetings and visits has been carried out by the London Branch of the Students Section during the first three months of 1935. Both meetings and visits have been very well attended.

Lubrication of Automobile Engines.

On Tuesday, 22nd January, a joint meeting was held with the Graduates Section of the Institution of Automobile Engineers at Bush House Restaurant, Aldwych. Mr. O. T. Jones, B.Sc., M.I.A.E., presented a Paper on "The Lubrication of Automobile Engines." Mr. Jones dealt with three functions of a lubricant—the reduction of friction, as a sealing medium for the pistons, and as a means of withdrawal of heat from the cylinders. From a consideration of the second of these functions, crankcase dilution and the relation between operating temperature and dilution were considered.

Mr. Jones described tests which had been carried out at the N.P.L. on the Jakeman Journal Friction test machine, and on the cold starting characteristics of heavy and light oils. Chassis lubrication was discussed in detail, and the requirements of special components, such as universal joints, synchromesh and preselective gearboxes, were considered from the point of view of co-operation between the petroleum technologist and the automobile engineer.

Determination of Cloud Point of Black Oils.

Mr. J. W. Hyde (Student) presented a Paper on the above subject at a meeting held at the Institution on Tuesday, 5th February. Mr. Hyde dealt with the significance of Cloud Point determinations, with particular reference to Diesel fuels and the effect of the thermal history of the oil on its Cloud Point. A method of determination based on the optical properties of the oil under examination was described, together with results obtained by the use of this method.

Efficiency of Modern Distillation.

On Tuesday, 19th February, after the conclusion of the Annual General Meeting, Mr. R. H. Keach, B.Sc. (Student), gave a survey of the features which contribute to the efficiency of modern distillation plant. The author dealt with the radiation and convection type of tube still and heat exchangers.

Structural Conditions of Oil Accumulation in Europe.

On Friday, 8th March, a successful symposium was held consisting of short Papers by students of the Royal School of Mines dealing with the structural

conditions of oil accumulation in Europe. The following students contributed to this symposium :

British Isles	H. S. ROGERS.
France	R. O. YOUNG.
Italy and Albania	A. J. HAWORTH.
Germany, Czechoslovakia, Austria and Hungary ...	S. E. COOMBER, A.R.S.M., B.Sc.
Poland	W. R. BOYD.
Rumania	R. E. DE MESTRE.

The Papers were illustrated by lantern slides.

Annual General Meeting.

The Annual General Meeting of the Branch was held on Tuesday, 19th February. After approval of the Annual Report for the Year Ended 31st December, 1934, for submission to the Council, the following were elected members of the Committee for the Session 1935–36 :

Messrs. A. S. BRIDGWATER, B.Sc., W. R. BOYD, E. J. FASOLA, B. C. FERGUSON, A. J. HAWORTH, R. H. KEACH, R. E. DE MESTRE, and W. R. WRIGHT.

Visits.

On Thursday, 10th January, by courtesy of Shell-Mex & B.P., Ltd., and the Shell Marketing Co., Ltd., an afternoon visit was made to the Shell Installations, Laboratories, etc., at Fulham. During the course of a comprehensive tour of the establishment the party visited the can- and drum-filling sheds, bulk storage, blending plant, motor repair centre, and the engine, road and chemical laboratories. An interesting series of demonstrations had been arranged in the laboratories and on the model road.

By courtesy of the Gas, Light & Coke Company a visit was made on Wednesday, 27th February, to the Beckton Gas Works. An instructive afternoon was spent in the inspection of the Company's coal handling plant, the coke ovens and the producer gas plant. Particular interest was taken in the new plant for the extraction of benzole from coal gas by activated carbon, which is designed to deal with 75 million cu. ft. of gas in 24 hours.

Annual Dinner.

The Annual Dinner of the London Branch was held at " Ye Olde Cock Tavern," Fleet Street, on Wednesday, 27th February. Mr. A. S. Bridgwater, B.Sc., Chairman of the Branch, presided. The toast of the Students Section was proposed by Mr. Ashley Carter, who referred to the fact that over 400 Students had passed through the Students Section since the inception of the Institution. Mr. B. C. Ferguson responded on behalf of the London Branch. The toast of the Institution was proposed by Mr. Bridgwater and replied to by Mr. C. Dalley. Mr. A. J. Haworth proposed the toast of Our Guests, and Mr. G. Sell replied.

RUMANIAN BRANCH.

At the 8th Annual General Meeting of the Rumanian Branch, held at Ploesti on 22nd February, 1935, the following were elected as office-bearers and members of the Committee for the ensuing year :—

Chairman :	PERCY R. CLARK.
Hon Treasurer :	CAPT. J. E. TREACY.
Hon. Secretary :	C. R. YOUNG.
Committee :	J. L. CHAILLET.
	I. EDELEANU.
	C. M. LEITCH.
	E. C. MASTERSON.
	F. W. PENNY.

CONTENTS OF APRIL JOURNAL.

The following Papers will be included in the April issue of the *Journal*:

" Notes on the Petroleum Geology of Western Canada." A. J. GOODMAN.

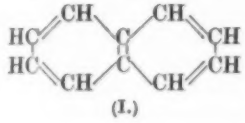
" Effects of Geophysical Factors in the Evolution of Oil and Coal." DAVID WHITE.

Report of Annual General Meeting

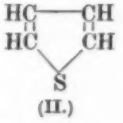
SULPHUR COMPOUNDS OF TECHNICAL INTEREST. THE ISOMERIC THIOPHTHENS.*

By Frederick Challenger and Jack Blatchley Harrison.

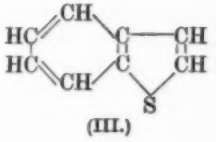
The occurrence of naphthalene (I), thiophen (II), and thionaphthen (III) in coal tar [1] and in Kimmeridge shale oil [2] suggested that thiophthen (IV) or (V) might also be an ingredient of bituminous oils. Attempts to detect this substance in coal tar and in lignite tar [3] were, however, unsuccessful. On the other hand, the published information concerning thiophthen and its derivatives is so scanty that success was hardly to be expected until these compounds had been further characterised. With this object in view the present investigation was commenced.



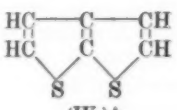
(I.)



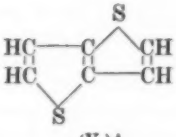
(II.)



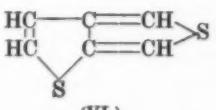
(III.)



(IV.)†



(V.)†



(VI.)

Thiophthen was first prepared by Biedermann and Jacobson,[4] who, employing an extension of the method devised by Victor Meyer for the preparation of thiophen and its homologues, heated citric or tricarballylic acids with phosphorus trisulphide. A tar distilled which, on fractionation, yielded an oil, b. p. 220–230°. This was purified through its picrate, m. p. 133°, which on decomposition with alkali gave an oil, b. p. 224–226°, which had the composition $C_6H_4S_2$ and remained liquid at −10°. The yield before picrate formation was less than 1 per cent. Treatment with bromine water gave a tetrabromothiophthen, m. p. 172°. Hanna and Smith [5] used aconitic acid and phosphorus trisulphide, obtaining a yield of thiophthen approximately equal to that given by the citric acid method.

Capelle [6] passed acetylene into the vapour of boiling sulphur and absorbed the distillate in carbon disulphide. Removal of the solvent, extraction with ether or alcohol and fractionation in the presence of sodium hydroxide yielded an oil, b. p. 225°, which gave a picrate, m. p. 134°, stated to be identical with that obtained by Biedermann and Jacobson. With bromine in dilute carbon disulphide a dibromothiophthen, m. p. 122·5°, was stated

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* Paper presented for discussion at the One Hundred and Sixty-second Meeting of the Institution of Petroleum Technologists, January 8th, 1935.

† Compounds (IV) and (V) may be systematically indicated as—thiopheno-2′ : 3′–2 : 3-thiophen and thiopheno-2′ : 3′–3 : 2-thiophen, respectively. The sulphur atom is numbered 1.

to be formed which with more bromine gave a tetrabromo-derivative, m. p. 172°, also mentioned by Biedermann and Jacobson. This, however, was not analysed. Another bromo-compound, m. p. 223°, was also described by Capelle which may be identical with the tetrabromothiophthen, m. p. 229–230°, obtained by Meyer and Wesche [7] by the bromination of a fraction, b. p. 215–232°, resulting from the pyrogenic condensation of a mixture of methane, acetylene and hydrogen sulphide, see p. 138. These authors regarded the last compound and that of m. p. 172° as dimorphous.

The interaction between acetylene and sulphur was investigated by Briscoe and Peel and by Peel and Robinson [8] at temperatures up to 600°. The average composition of the distillate was found to be carbon disulphide 77 per cent., thiophen 9–12 per cent., thiophthen 6 per cent. (The statement by Capelle and by de Coninck [9] that thiophen is absent from the products of this reaction is doubtless due to the relatively small quantities with which they worked, see p. 141.) Distillation under reduced pressure gave a fraction, b. p. 110–115°, at 20 mm. with the reactions of thiophthen. (No analysis is given nor any other data of identification, nor was the specimen submitted to any further purification, the main interest of the authors being directed towards other aspects of the investigation.)

In this connexion the work of Friedmann [9a] should be mentioned. He found that on heating *n*-octane or octylene (methyl-*n*-amylethylene) with sulphur under pressure at 270–280° a liquid thiophen homologue $C_8H_{12}S$ and a 2 per cent. yield of a compound $C_8H_8S_2$, m. p. 116–117°, were obtained. The latter formed very large, colourless, monoclinic crystals of micaceous appearance which gave a red picrate, m. p. 127°. They also gave the indophenin reaction and an intense yellowish-green fluorescence in sulphuric acid. The thiophthens also exhibit a similar fluorescence (see p. 142). Bromination gave a dibromo-substitution product, and Friedmann regarded the compound as a dimethylthiophthen.

It appeared probable that large quantities of thiophthen would be required for the preparation and study of derivatives which could ultimately be used in the identification of this compound; moreover, it was proposed to investigate the oxidation and reduction of thiophthen and compare its behaviour with that of thiophen and thionaphthen.[10] It was therefore determined to use the method of Capelle for the preparation of thiophthen, since that of Biedermann and Jacobson, using citric acid, gave a very poor yield which it was not found possible to improve.

Acetylene was passed in a rapid stream into the vapour of boiling sulphur. The crude distillate, freed from carbon disulphide and thiophen, was distilled in steam and that portion of the distillate of b. p. 115–120° at 20 mm. converted to picrate of m. p. 139–141° and this decomposed with sodium carbonate giving a colourless oil, b. p. 221–222° (102–104° at 15 mm.). Its analysis agreed with that of slightly impure thiophthen. On standing it gradually deposited a solid which on crystallisation from light petroleum melted at 56°, had a composition and molecular weight corresponding to $C_6H_4S_2$ and gave a picrate $C_6H_4S_2 \cdot C_6H_2(NO_2)_3OH$ of constant m. p. 145°. No mention of this solid compound is made by the earlier workers who employed the acetylene method for the preparation of thiophthen. It may here be mentioned (see also p. 139) that Anschütz and Rhodius [11] directed attention to the theoretical existence of two isomeric thiophthens (IV) and (V).

The liquid portion (S) was repeatedly frozen, but its sulphur content (43·7 per cent. instead of 45·8 per cent.) showed that it was not pure thiophthen. It was converted to the styphnate which, on repeated crystallisation from methyl alcohol, had a m. p. 126°, turning black. This treatment removed all remaining solid thiophthen, the styphnate of which is easily soluble in methyl alcohol. Decomposition of the styphnate with sodium carbonate gave a liquid (S_1) which still contained some impurity, since, unlike either solid thiophthen (T) m. p. 56° or liquid thiophthen (C) prepared from citric acid, it gave immediately a black solid with saturated aqueous mercuric chloride and more slowly a white mercuration product. (T) and (C) give only white mercurated compounds on standing. (S_1) readily formed a picrate which had constant m. p. 138–139°, turning black. The important point should here be emphasised that the picrate and styphnate of the pure liquid thiophthen (C) melt at 136–137° and 129·5–130·5° respectively and show no trace of blackening on fusion.

Since it appeared that the black solid obtained with mercuric chloride might be derived from an impurity, the whole of the oil regenerated from the styphnate was treated with this reagent. The unchanged oil (S_2) was extracted from the blackened mixture. It then gave a picrate and a styphnate m. p. 138–139° and 128–129° respectively, each compound giving a clean yellow melt. Comparison with the corresponding compounds prepared from (C) still revealed a slight but definite difference in m. p. This result was surprising and indicated the presence of a small quantity of some tenaciously adhering impurity in (S_2), a conclusion confirmed by the analysis of the oil itself.

The difficulty experienced in the separation of this impurity indicated that it must be of a similar nature to thiophthen. It had been shown by Voerman,[12] that the α- and β-thiophencarboxylic acids form mixed crystals which are not separable on crystallisation; the same is, of course, true of benzene and thiophen and of several pairs of picrates derived from naphthalene, the α- and β-methylnaphthalenes, thionaphthen and thiophthen derived from citric acid.[13]

Attempts to purify the liquid thiophthen (S_2) by recrystallisation from light petroleum below 0° were unsuccessful. The presence of a trace of thionaphthen as impurity suggested itself, especially as some evidence of the presence of this compound was obtained by Meyer and Meyer [14] in a study of the products of the pyrogenic condensation of acetylene and hydrogen sulphide. In 1926 Mr. R. J. Bramhall, M.Sc., working in the laboratory of one of us at the University of Manchester, had shown that thiophthen (C) obtained by the citric acid method (kindly prepared and purified by Miss V. K. Wilson, M.Sc.) readily reacted with cold alcoholic mercuric chloride, whereas thionaphthen was unaffected under these conditions and could thus be recovered from a mixture with thiophthen (see pp. 144 and 148).

The whole of the oil (S_2) was therefore fractionally mercurated, whereby a few centigrams of oil remained unchanged, and was identified as thionaphthen by m. p. 31–32° and analysis, and by the m. p. and analysis of the picrate and styphnate, the figures being 148–149° and 136–137° respectively. It is of interest that a compound, m. p. 31°, was isolated by Capelle in his experiments and, although he performed no analysis, he

regarded it as being probably thionaphthen. Decomposition of the mercurichloride obtained in the above treatment with hydrochloric acid yielded an oil (S_3) which on analysis was found to be a pure liquid thiophthen. The picrate and styphnate melted, however, at 137–138° and 127–128°, whereas the figures for the carefully purified products from (C) are 136–137° and 129·5–130·5° respectively. No marked depression in m. p. occurred on mixing, the observed figures being 136–138° and 127–130°. This does not, however, necessarily indicate the identity of (C) and (S_3) (see p. 150), and in view of the behaviour of the derivatives now to be described, we were inclined to regard these two thiophthens as distinct individuals which, with the solid thiophthen of m. p. 56°, would make three isomeric thiophthens of the formula $C_6H_4S_2$. The m. p.'s of (C) and (S_3) were determined in the apparatus described by Stock [15] and found to be 5·75–6·0° and 6·25–6·5° respectively.

In order to obtain evidence as to the identity or otherwise of the products (C) and (S_3) and to characterise the solid thiophthen (T), these were separately converted to the mononitro-derivatives and the methyl ketones. Nitration was effected in acetic anhydride as in the case of thiophen [16] and the ketones were obtained by interaction with acetyl chloride in carbon disulphide in the presence of stannic chloride instead of aluminium chloride.[17] The corresponding *p*-nitrophenylhydrazones and 2 : 4-dinitrophenylhydrazones were also prepared. The m. p.'s are tabulated below, also those of the picrates and styphnates and the various mixed m. p.'s.

Compound.	Thiophthen (C).	Thiophthen (S).	Mixed m. p.
Picrate	136–137°	137–138° (S_3)	136–138°
Styphnate	129·5–130·5°	127–128° (S_3)	127–130°
Methyl ketone	115–116°	113° (S_3)	113–115°
p-Nitrophenylhydrazone	241–242°	241–242°	241–242°
2 : 4-Dinitrophenylhydrazone	267–268°	267–268°	267–268°
Mononitro-derivative	122–123°	125·5–126° (S_3)	124–125°
Tribromo-compound	123–124°	123–124°	123–124°

It will be noticed in the above table that, in the case of the liquid thiophthen obtained from acetylene, some of the compounds were prepared from thiophthen which had not been completely purified. However, this does not affect any conclusions that may be drawn from the above data, since all the compounds were of constant m. p. and gave excellent results on analysis. Furthermore, since more of the pure thiophthen (S_3) has been available, both the ketone and the nitro-compound have again been prepared in the course of further investigations and have been found to have exactly the same m. p., 113° and 125·5–126°, as when prepared from (S_2).*

* The possibility that the discrepancies in m. p. might be due to the presence of traces of solid thiophthen is extremely remote in view of the undoubted efficiency of the purification of (S) by styphnic acid (see p. 143). The presence of solid thiophthen (T) in (S) is easily demonstrated on bromination (p. 148) when the tetrabromo-derivative of solid thiophthen (T), which is very insoluble in alcohol, contaminates the tribromo-derivative of liquid thiophthen. On bromination of (S_1) this was not observed, and it should be noticed that all the above derivatives were obtained from the still more highly purified products (S_2) and (S_3).

On bromination in carbon disulphide both the liquid thiophthens yielded tribromo-derivatives of m. p. 123–124°, which is a figure very close to that (122·5°) recorded by Capelle [18] for his dibromothiophthen. Solid thiophthen gave a tetrabromo-derivative, m. p. 230–231°, probably identical with those of m. p. 223° and 229–230° described by Capelle and by Meyer and Wesche.

Solid Thiophthen, m. p. 56°.—The physical constants of the compounds prepared from solid thiophthen may now be recorded.

Compound.	Solid (T).	Mixed with (C).	Mixed with (S).
Picrate	145°	139–141°	139–141°
Styphnate	112–113°	115–116°	115–116°
Methyl ketone	126–127°	105°	105°
2 : 4-Dinitrophenylhydrazone	267°	—	260°
p-Nitrophenylhydrazone	246–247°	238°	238°
Mononitro-compound	124·5–125°	122–125°	124·5–126°
Tetrabromo-derivative	230–231°	—	—

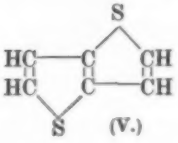
The Reduction of the Thiophthens.—The reduction of the solid thiophthen (T) with sodium and alcohol causes fission of the molecule with the formation of a mercaptan. A similar phenomenon was noted by Fricke and Spilker,[19] who obtained dihydrothionaphthen and *o*-ethylthiophenol by reduction of thionaphthen under analogous conditions. The mercaptan from (T) gave a mercury derivative, m. p. 76–77°, with the composition of an ethylthiophen mercury mercaptide $(Et{\cdot}C_4H_2S)_2Hg$. The two liquids (C) and (S_2) on reduction also gave an intense mercaptan odour. The properties and synthesis of these mercaptans are still under investigation.

The Structures of the Thiophthens.—An X-ray analysis of the pure solid thiophthen crystals kindly undertaken by Dr. Bernal of Cambridge showed the compound to have a centre of symmetry. A determination of the dipole moment carried out by Dr. Goss of the Organic Chemistry Department of the University of Leeds gave a zero value. These facts agree perfectly with the structure (V) for solid thiophthen, and it will be noted that reduction (p. 149) would result in the formation of 2-ethyl-3-mercaptothiophen.

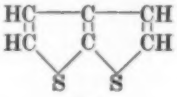
In the case of the liquid thiophthens (C) and (S_3) it was at first thought that these would prove to be identical, but the difference in m. p. obtained for several analogous derivatives cast doubt upon this. Dr. Goss kindly undertook the investigation of the dipole moment of the two liquids also. His first experiments indicated that the liquid thiophthen (S_3) still contained a minute trace of impurity which was removed by further fractional mercuration with saturated alcoholic mercuric chloride followed by regeneration of thiophthen (S_4) from the resulting mercurichloride. The densities of the two liquids in 2·5 per cent. concentration in heptane were the same but the dielectric constants were different. The dipole moments calculated from this data, without, however, making any allowance for association or the anisotropy of the polarisation field,[19a] were 1·16 for the thiophthen (C) and 1·03 for the thiophthen (S_4). These values are of the same order of magnitude as the value 1·17 calculated for the structure (IV)

by the method of vectorial addition [19b] using the value 0·63 obtained for thiophen by Naeshagen and Hassel [19c] but without making any allowance for induced polarities.[19d] The structure (VI) may also be expected to have a dipole moment of the same order of magnitude.

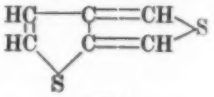
Thus in the light of the results obtained it is possible that the two liquids are different entities. The evidence from the dipole moments is consistent with their formulation as the structures (IV) and (VI) or possibly as mixtures of these. From the action of phosphorus trisulphide on citric acid the formation of (IV) is easy to understand. The C-skeleton of citric acid may, however, be written consequently the formation of (VI) is also possible. It is hoped to present more conclusive evidence regarding the relations of (C) and (S_4) in a later communication.



(V.)



(IV.)



(VI.)

On the reduction of the methyl thiophthienyl ketones, m. p. 126–127° and 113°, obtained from the solid thiophthen (T) and from the liquid thiophthen (S_2) (see p. 137) by Clemmensen's method [20] two liquid ethylthiophthens, b. p. 120° and 120–125° at 15 mm., were obtained. The first contained a trace of impurity, but the second was quite pure. The corresponding picrates melted at 65° and 70° and were extremely soluble in methyl alcohol. The presence of the second ethylthiophthen in crude thiophthen (S_2) would thus appear to be excluded.

The methyl ketone obtained from the liquid thiophthen (S_3) was oxidised with potassium hypobromite, but instead of the corresponding acid two bromo-derivatives of the thiophthencarboxylic acid were obtained. These, on distillation with lime, gave a mixture of brominated thiophthens. The use of potassium ferricyanide as oxidising agent gave a thiophthen carboxylic acid of m. p. 239–240°, which when distilled with lime gave a liquid thiophthen of which the picrate after two crystallisations had the m. p. 136·5–137·5° * as compared with that of the original thiophthen (S_3) (137–138°) and that of thiophthen (C) (136–137°). This attempt to prove the identity of the two liquid thiophthens by the removal of traces of impurity from (S_3) was therefore unsuccessful.

The purest liquid thiophthen from the sulphur–acetylene reaction (S_3) was converted to the mononitro-derivative, which was reduced by stannous chloride and hydrochloric acid,[21] and the amine converted without isolation to the acetyl derivative $C_6H_3S_2{\cdot}NH{\cdot}COCH_3$, m. p. 220·5–221·5°.

The methyl ketones from (T) and (C) (see p. 152) gave oximes of m. p. 172–173° and 160–161° respectively.

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* The quantity was too small for further crystallisation, so the constancy of the m. p. cannot be claimed. The three m. p.'s mentioned were taken simultaneously.

Experimental.

Preparation of solid and liquid thiophthens from acetylene and boiling sulphur.

The apparatus was a modified form of that used by Peel and Robinson.[22] The acetylene was obtained from a cylinder of the compressed absorbed gas, and before reaching the sulphur was passed by one arm of a T-piece through strong sodium hydrogen sulphite solution to remove some of the acetone. Complete removal was not attempted. The gas was washed with water and dried by passing through calcium chloride and soda lime.

The crushed roll sulphur (1000 gs.) was contained in a Pyrex flask of two litres capacity. The tube taking the acetylene into the reaction flask was of wide bore and passed to the centre of the vessel, thus giving a good supply of gas at the surface of the boiling sulphur. The Pyrex flask was well lagged with asbestos board and heated by means of a ring burner. Throughout the many runs performed in this apparatus, at no time did the reaction flask break. Breakage occasionally occurred in removing the carbonaceous matter after the experiment, especially if a cake of sulphur remained. If the sulphur completely volatilised, a flask could be used thrice before cleaning, which was then effected by heating with concentrated nitric acid. The reaction flask was connected by its side arm and a water-soaked asbestos-wool joint to a litre bolt-head flask cooled in a constant level water bath, and provided with an efficient condenser leading by a long tube to a flue.

Coal gas, introduced by the T-piece, was passed freely through the apparatus to remove all the air and so avoid explosion. The sulphur was gently heated till fusion was complete and then more strongly, the coal gas being stopped and a steady and rapid stream of acetylene introduced. When the sulphur boiled, the acetylene burned in its vapour with a red flame which filled the flask, giving a brown smoke. A black deposit formed on the walls and a dark tar-like liquid condensed in the receiver. Large quantities of hydrogen sulphide passed on. The use of a second receiver effected practically no further condensation. With 1000 gs. of sulphur, 170–200 c.c. of distillate were obtained. This was heated to 100° until nothing further passed over, and the residue distilled in steam giving an orange-coloured oil and a thick non-volatile tar, which has not been further examined. That portion volatile below 100° was mostly carbon disulphide, but contained some thiophen (see p. 136). In the earlier experiments the oil volatile in steam was fractionated at ordinary pressures, that portion of b. p. 220–230° converted to picrate which was crystallised to constant m. p. 139–141° and decomposed by sodium carbonate. The resulting oil distilled entirely from 221–224°, and on cooling deposited a solid, m. p. 48–49°, which was raised to 56° on recrystallisation from light petroleum, b. p. 40–60°. This method was later discarded in favour of the following:—

The whole of the product volatile in steam was distilled at 100 mm., then as the b. p. rose at about 40 mm. and finally at 15 mm. The fractionation need not be recorded in detail, but three sets of typical figures may be given.

13,300 gs. of sulphur gave 520 gs. of oil volatile in steam, of which 264 gs. boiled from 97–120° at 15 mm.; 3000 gs. of sulphur gave 200 gs. of oil, of which 102 gs. boiled within these limits; finally, in a third series the corresponding figures were 8000, 347 and 205.

In all 32 kilograms of sulphur were employed, but records of yields apply only to the case of the last 24 kilograms. The lower and higher fractions, ranging from 22° at 50 mm. to 164° at 15 mm., were only superficially examined. All fractions contained varying amounts of mercaptans as seen by the formation of yellow compounds with solid lead acetate. The lowest fractions contained thiophen or its homologues as indicated by the indophenin reaction, but the relatively small quantity has so far not justified attempts to isolate them.

The fractions of b. p. 105–120° at 15 mm. deposited crystals of m. p. 48–49°. A further quantity was obtained on cooling. The total solid was recrystallised once from light petroleum (yield 65 gs.) and the mother-liquors evaporated and added to the liquid portion of the original oil.

The conversion of the oil to picrate was carried out in small convenient proportions, but in all 395 gs. of oil in hot methyl alcohol were treated with a hot solution of 760 gs. (a slight excess of the calculated quantity) of picric acid in the same solvent. On cooling, orange needles of constant m. p. 139–141° were obtained (861 gs.), the melt turning black. Concentration of the mother-liquors yielded a further quantity (130 gs.) of impure, discoloured picrate, m. p. 135° (blackening). On evaporation of the filtrate to dryness 215 gs. of a dark residue were obtained. The crude picrate, m. p. 135°, was decomposed with sodium carbonate in steam and the resulting oil treated with 90 gs. of picric acid in methyl alcohol, giving a further 125 gs. of picrate, m. p. 139–141° (blackening), and 8 gs. of impure residues. The pure picrate (986 gs.) was similarly decomposed in steam in lots of 200 gs., giving a heavy almost colourless oil (344 gs.). A further 5 gs. were obtained on the ether extraction of the water layer. Total yield 349 gs. (P). (From the picrate residues (223 gs.) 61 gs. of a dark oil were obtained, b. p. 110–150 at 15 mm.) On fractionation at 15 mm. practically the whole (316 gs.) of this oil (P) boiled at 104–106°; a higher fraction (29 gs.) had b. p. 105–110° at 13 mm. The 316 gs. of oil were repeatedly frozen at 0° and three deposits of solid removed. These were mixed with the solid (65 gs.) obtained from the main fraction before treating with picric acid. Recrystallisation from light petroleum yielded in all 136 gs. of snow-white solid, m. p. 51–52°, which on further crystallisation was raised to 56°.

4·825 mgs. gave 9·05 mgs. CO_2 and 1·30 mgs. H_2O; C = 51·24, H = 3·0.
13·101 mgs. gave 43·25 mgs. $BaSO_4$; S = 45·32.
0·2108 g. in 18·853 gs. of benzene gave a depression of freezing-point 0·405°. Hence Mol. Wt. = 138·1.
$C_6H_4S_2$ requires C = 51·4, H = 2·9, S = 45·8 per cent. Mol. Wt. = 140.

The solid gave a picrate of constant m. p. 145°.

13·166 mgs. gave 16·430 mgs. of $BaSO_4$; S = 17·15.
3·156 mgs. gave 0·300 c.c. of N_2 at 22° and 757 mm.; N = 11·2.
$C_6H_4S_2 \cdot C_6H_2(NO_2)_3OH$ requires S = 17·35, N = 11·4 per cent.

Solid thiophthen gives a purplish-blue indophenin reaction and a strong greenish fluorescence with sulphuric acid which is best observed with very small quantities of the sulphur compound. The reddish-brown colour produced with larger amounts masks the fluorescence. This is also true

of the liquid thiophthens (C) and (S). With phosphorus pentoxide solid thiophthen gives a purple colour becoming blue. This was first observed on keeping thiophthen in a desiccator over the pentoxide. Water discharges the colour which is possibly due to the formation of a sulphonium salt. A similar but less intense colour is produced on warming with syrupy phosphoric acid.

Solid thiophthen does not blacken with aqueous mercuric chloride, and only very slowly gives a violet colour with the solid salt. Anhydrous thallic chloride gives a bluish-purple colour which quickly darkens giving an almost black solid. The nature of these coloured products obtained from thiophthen and similar compounds with inorganic halides is now under investigation.

That portion of the oil which remained liquid in ice (200 gs.) was designated (S) and its methyl-alcoholic solution treated in three portions with a methyl-alcoholic solution of styphnic acid yielding 414 gs. of pale yellow styphnate, m. p. 126° (blackening). The mother-liquors were evaporated, yielding 181 gs. of dark-coloured residue from which the impure thiophthen was regenerated (see below). The pure styphnate (414 gs.) was decomposed with sodium carbonate in steam and the volatile oil separated. It distilled constantly at 102·9–103·9° at 13 mm. (S_1), was clear and colourless but darkened after a few days. It had a clean odour like the solid thiophthen (T). Weight 140 gs.

15·308 mgs. gave 49·23 mgs. $BaSO_4$; S = 40·7.
$C_6H_4S_2$ requires S = 45·8 per cent. It was therefore not pure thiophthen.

The oil regenerated from the styphnate residues was fractionated and yielded 57 gs. of b. p. 102·9° at 13 mm. This deposited a large amount of solid thiophthen at room temperature, which proved the efficiency of the styphnic acid treatment in removing this product from the oil (S), which before conversion to styphnate was entirely liquid at 0°. The styphnate of solid thiophthen (T) is very soluble in methyl alcohol, hence the separation. For this reason the use of styphnic acid is to be preferred to that of picric acid at this stage of the purification.

As a result of the treatment just described there was obtained from 24,300 gs. of sulphur 374 gs. of thiophthen consisting of 136 gs. of solid (T), 140 gs. of liquid thiophthen (S_1) containing about 10 per cent. of impurity, and 98 gs. of a mixture of solid and liquid. It appears, therefore, that the solid and liquid thiophthen are produced in equal amounts, as would be expected from a consideration of the interaction of acetylene and sulphur. The total yield of the two isomers is only 15·5 gs. per 1000 gs. of sulphur.

Purification of the Liquid Thiophthen (S_1) with Mercuric Chloride.

It was hoped to convert the oil to a mercurichloride which might be purified by crystallisation as in the case of thiophen and its homologues,[23] and then decomposed with acid to regenerate pure liquid thiophthen. The simple process of mercuration was, however, accompanied by a side reaction due to the impurity present.

The oil (S_1) (40 gs.) was shaken with 150 c.c. of saturated mercuric chloride (aqueous) and left for 30 minutes. The liquid was decanted and the now blackened oil treated with a further 150 c.c. of mercuric chloride and left to stand till the formation of a white thiophthen mercurichloride commenced. Unchanged oil was then extracted with light petroleum, washed, dried and distilled, giving 33 gs. of b. p. 103·2–104° at 13 mm. This was left with 300 c.c. of mercuric chloride overnight, further blackening being observed. Extraction as before yielded 28 gs. of b. p. 104–105° at 13 mm. This underwent no further blackening with aqueous mercuric chloride and was then treated with 2 gs. of solid mercuric chloride which produced an immediate violet colour (the origin of which is under investigation) and an odour of hydrogen chloride. This drastic treatment was employed for only 10 minutes, after which extraction with light petroleum yielded 26 gs. of oil of b. p. 101° at 12·5 mm. (S_2), which gave no colour with solid mercuric chloride, had a clean odour and remained quite colourless on keeping.

4·68 mgs. gave 9·05 mgs. CO_2 and 1·31 mgs. H_2O; C = 52·75, H = 3·13.
20·552 mgs. gave 65·83 mgs. $BaSO_4$; S = 43·96.
0·3614 g. in 22·99 gs. benzene gave a depression of the freezing-point of 0·6°. Mol. Wt. = 131.
$C_6H_4S_2$ requires C = 51·4; H = 2·8; S = 45·8 per cent. Mol. Wt. = 140.

This preparation gave a pale yellow picrate of constant m. p. 138–139° and a pale yellow styphnate of constant m. p. 128–129°. No blackening occurred in either case on fusion. Hence, although the impurity causing blackening of the picrate and styphnate on melting and giving a black solid with mercuric chloride had been removed, there still remained some impurity which owing to its persistence must be very closely related to thiophthen.* It appeared possible that this might be thionaphthen, and calculation showed that a mixture of 92 per cent. thiophthen and 8 per cent. thionaphthen would give the observed sulphur content of 44 per cent. Moreover, a mixture of approximately 92 per cent. of thiophthen picrate from citric acid (p. 146) and 8 per cent. of thionaphthen picrate [24] was found to have a m. p. of 138–139°, unchanged by crystallisation.

Since thionaphthen does not react with cold alcoholic mercuric chloride the following method of purification was attempted. The liquid thiophthen (S_2) (10·7 gs.) in a little alcohol was treated with 85 c.c. of saturated alcoholic mercuric chloride. A white crystalline solid separated overnight (2·1 gs.). This was recrystallised from 250 c.c. of a benzene–acetone mixture (1 : 1) giving 1·8 gs. of small white crystals unmelted at 300°.

12·12 mgs. gave 14·7 mgs. $BaSO_4$; S = 16·8.
$C_6H_3S_2ClHg$ requires S = 17·1 per cent.

The mercurichloride was decomposed with hydrochloric acid in steam giving 0·7 g. of oil which was removed with light petroleum. It distilled at 98° at 13 mm. and readily solidified in ice (S_3). Its m. p. was determined by the method of Stock [24a] using an apparatus kindly loaned by

* The black solid is at present under investigation.

Dr. Denbigh of the Department of Inorganic Chemistry of the University of Leeds. The m. p. was 6·25–6·5°.

4·831 mgs. gave 9·100 mgs. CO_2 and 1·410 mgs. H_2O; C = 51·4, H = 3·2.
17·181 mgs. gave 57·455 mgs. $BaSO_4$; S = 45·9.
$C_6H_4S_2$ requires C = 51·4, H = 2·9, S = 45·8 per cent.

The product (S_3) was therefore pure liquid thiophthen. Its picrate and styphnate crystallised from methyl alcohol, melted constantly at 137–138° and 127–128°.

The alcoholic mercuric chloride mother-liquor remaining after the separation of the 2·1 gs. of pure thiophthen mercurichloride was diluted with water whereby 8·5 gs. of oil, b. p. 100° at 15 mm., were recovered. An analysis of this showed, as was expected, an accumulation of the impurity, the sulphur content being 43·8 instead of 45·8. The m. p. of the picrate and styphnate were slightly too high, namely 138–139° and 128°. This oil was fractionally treated (four times) with saturated alcoholic mercuric chloride containing 20 per cent. of water in such a manner that the deposited solid was removed each time and unchanged oil, thrown out by the addition of water, again treated as before. In all 14 gs. of mercurichloride were obtained which, with hydrochloric acid, yielded 3·7 gs. of oil of b. p. 101–102° at 17 mm.

14·960 mgs. gave 50·020 mgs. $BaSO_4$; S = 45·9. $C_6H_4S_2$ requires S = 45·8 per cent.

This represents the purest liquid thiophthen obtained up to this stage. The alcoholic mother-liquors from the successive deposits of mercurichloride yielded finally 0·3 g. of unattacked oil, which, from the m. p. of the picrate and styphnate, was a mixture.

A repetition of this laborious process of fractional mercuration using 27 gs. of oil (S_2) finally yielded 0·45 g. of unreacted oil, b. p. 100° at 16 mm., with the odour of thionaphthen, which solidified in ice and then had m. p. 31–32° alone and in admixture with pure thionaphthen (m. p. 31–32°).

5·20 mgs. gave 13·62 mgs. CO_2 and 2·20 mgs. H_2O; C = 71·45, H = 4·7.
8·719 mgs. gave 14·67 mgs. $BaSO_4$; S = 23·1.
C_8H_6S requires C = 71·6, H = 4·5, S = 23·9 per cent.

A portion of the thionaphthen thus isolated was converted to the picrate, m. p. and mixed m. p. 148–149°, with authentic thionaphthen picrate, m. p. 148–149°.

4·985 mgs. gave 8·455 mgs. CO_2 and 1·140 mgs. H_2O; C = 46·3, H = 2·56.
11·862 mgs. gave 7·525 mgs. $BaSO_4$; S = 8·7.
2·953 mgs. gave 0·294 c.c. N_2 at 23° and 759 mm.; N = 11·5.
$C_8H_6S{\cdot}C_6H_2(NO_2)_3OH$ requires C = 46·3, H = 2·5, S = 8·8, N = 11·56 per cent.

The corresponding styphnate was also prepared and had m. p. and mixed m. p. 136–137° with authentic thionaphthen styphnate, m. p. 136–137°.

4·555 mgs. gave 7·36 mgs. CO_2 and 1·03 mgs. H_2O; C = 44·1, H = 2·53.
10·308 mgs. gave 5·940 mgs. $BaSO_4$; S = 7·9.

2·771 mgs. gave 0·266 c.c. N_2 at 25·5° and 765 mm.; N = 11·0.
$C_8H_6S{\cdot}C_6H(NO_2)_3(OH)_2$ requires C = 44·3, H = 2·4, N = 11·1, S = 8·4 per cent.

The collected mercurichloride deposits obtained from the 27 gs. of (S_2) used in this process gave 16 gs. of oil (S_3), b. p. 106° at 16 mm.

4·870 mgs. gave 9·090 mgs. CO_2 and 1·42 mgs. H_2O; C = 50·9, H = 3·26.
21·833 mgs. gave 73·035 mgs. $BaSO_4$; S = 45·9.
$C_6H_4S_2$ requires C = 51·4, H = 2·9, S = 45·8 per cent.

This specimen was used by Dr. Goss (see p. 139) in the determination of the density whereby the presence of a trace of impurity was detected. 10 gs. were therefore once again fractionally treated with saturated alcoholic mercuric chloride until 8 gs. of mercurichloride had been accumulated. Decomposition of this yielded a product (S_4). The measurement of density gave a figure almost identical with that of (C).

Preparation of Liquid Thiophthen (C) from Citric Acid and Phosphorus Trisulphide.

Since this method was stated to give very low yields, attempts were made to replace the citric acid by sodium or potassium citrate, or by ethyl citrate, but under these conditions no thiophthen was obtained. The method of Biedermann and Jacobson [25] was therefore employed, slightly modified as follows :—

A mixture of finely powdered anhydrous citric acid (75 gs.) (dehydrated at 150°), dried silver sand (20 gs. to minimise frothing) and well-powdered phosphorus trisulphide (150 gs.) was placed in a 2-litre round-bottom flask immersed in an oil bath and connected to two filter flasks containing a little water, to a third containing sodium hydroxide solution, and finally to a soda–lime tower. On raising the temperature of the bath to 140° fuming began, which gradually increased till at 220–230° a violent reaction occurred. Brown fumes were evolved and a small amount of a brown viscous oil collected in the first receiver. Much hydrogen sulphide was evolved and the contents of the flask frothed up to four times their original volume. The temperature was raised to 270°, when a few more drops of oil came over. The accumulated product from seventeen experiments was distilled in steam and the orange oil (8 gs.) so obtained heated in hot methyl alcohol with a saturated solution of styphnic acid in the same solvent, whereby 10 gs. of a pale-yellow styphnate of constant m. p. 126° were obtained. This was decomposed with sodium carbonate in steam giving a colourless oil with the characteristic thiophthen odour which boiled constantly at 220–221°. It was converted to the picrate, m. p. 136–137°, from methyl alcohol (Biedermann and Jacobson give m. p. 133° for their preparation). This picrate (0·5 g.) was decomposed in steam as before, giving an oil, which was again converted to styphnate in methyl alcohol, when a product of constant m. p. 129·5–130·5° was obtained.

10·91 mgs. gave 13·06 mgs. $BaSO_4$, whence S = 16·45.
3·02 mgs. gave 0·275 c.c. N_2 at 21·5° and 762 mm.; N = 10·6 per cent.
$C_6H_4S_2{\cdot}C_6H(NO_2)_3(OH)_2$ requires S = 16·66, N = 10·9 per cent.

On one occasion a batch of phosphorus trisulphide was obtained which did not react with citric acid, although apparently of high quality. Addition of a small quantity of free sulphur caused a normal reaction.

Slightly better yields of (C) were more quickly obtained using citric acid (20 gs.), phosphorus trisulphide (35 gs.) and sulphur (2 gs.), omitting sand, in a 250-c.c. flask, the oil bath being first heated to 150°. In this way a large number of charges could be quickly manipulated. The subsequent operations were the same as above, the b. p. of the pure product being 99–100° at 12 mm.

4·958 mgs. gave 9·345 mgs. CO_2 and 1·300 mgs. H_2O; C = 51·43, H = 2·93.

12·730 mgs. gave 42·225 mgs. $BaSO_4$; S = 45·55.

0·2998 g. in 21·035 gs. benzene gave a depression of the freezing-point of 0·567°. Mol. Wt. = 125·3.

$C_6H_4S_2$ requires C = 51·3, H = 2·9, S = 45·8 per cent. Mol. Wt. = 140.

The m. p. was determined in Stock's apparatus (see p. 144) and three readings gave the same figure, 5·75–6·0°.

Isolation of a By-product in the Preparation of Liquid Thiophthen (C).

The product obtained from another 20 runs (from 1500 gs. of citric acid) was distilled in steam as before, but in this case fractionated at 16 mm., when a small quantity of oil, b. p. 120–140°, was obtained, which solidified in a freezing mixture. After pressing on tile a solid of m. p. 75–81° was obtained which crystallised from alcohol in pinkish needles of m. p. 86–87°. These did not react with mercuric chloride and formed no picrate in methyl alcohol.

4·56 mgs. gave 7·745 mgs. CO_2 and 1·120 mgs. H_2O; C = 46·31, H = 2·75.

10·932 mgs. gave 32·560 mgs. $BaSO_4$; S = 40·96. By difference O = 10·00.

0·277 mgs. and 0·451 mgs. in 3·85 mgs. and 5·90 mgs. camphor respectively gave depressions of 17° and 18·1°. Mol. Wt. = 169 and 162.

$C_6H_6S_2O$ requires C = 46·15, H = 3·2, S = 40·5, O = 10·13 per cent. Mol. Wt. = 158.

$C_6H_4S_2O$ requires C = 46·13, H = 2·7, S = 41·03, O = 10·26 per cent. Mol. Wt. = 156.

The composition of $C_6H_4S_2O$ suggests a hydroxy-thiophthen and the substance was found to show some of the properties of a phenol, *e.g.*—

(1) It is readily soluble in cold sodium hydroxide, the solid at first turning red. The reason for the colour change is not readily apparent.

(2) Addition of benzenediazonium chloride to the alkaline solution gives a dark red precipitate.

(3) The compound is sparingly soluble in water and the resulting solution gives a green precipitate with ferric chloride as does β-naphthol.

The quantity of this substance was not sufficient for a more detailed examination.

Mercuration of Liquid Thiophthen (C).—A few drops of thiophthen from the decomposition of the pure picrate were added to about 10 c.c. of

saturated alcoholic mercuric chloride and left for 2 days. A crystalline solid unmelted at 280° was deposited and recrystallised from a mixture of benzene and acetone. It was free from calomel and gave an indophenin reaction similar to that exhibited by thiophthen.

0·0321 g. gave 0·0198 g. HgS; Hg = 53·27.
$C_6H_3S_2$·HgCl requires Hg = 53·40.

The above mercurichloride (0·06 g.) was boiled with sodium iodide (0·3 g.) in the minimum quantity of acetone for 5 minutes. A precipitate of sodium chloride was formed and after standing for 1 hour was separated, the acetone removed from the filtrate, and the residue treated with water to dissolve inorganic salts. The insoluble residue was recrystallised from alcohol and found to be halogen-free. On heating it gradually decomposed above 220°.

0·0249 g. gave 0·0121 HgS; Hg = 41·76.
$C_{12}H_6S_4Hg$ requires Hg = 41·84 per cent.

The compound was evidently a mercury dithiophthienyl $Hg(C_6H_3S_2)_2$ and reacted with mercuric bromide in acetone to give a product containing halogen, which was recrystallised from alcohol. The amount of this compound, presumably thiophthen mercuribromide $C_6H_3S_2$·HgBr, was too small for further investigation (see Steinkopf,[26] for similar reactions with mercurated thiophen compounds).

Oxidation of Thiophthen (C) with Potassium Permanganate.

Thiophthen (5 drops) was added to aqueous 4 per cent. potassium permanganate solution (50 c.c., sulphate free) and shaken mechanically. Decolorisation was effected in 3 hours, and after addition of two further quantities of 50 c.c. oxidation was complete. Excess permanganate was removed by alcohol, the manganese oxide separated and washed with alcohol. On concentration, the filtrate showed the presence of sulphate with acid barium chloride. Oxalate was absent. Extraction of the evaporated filtrate and of the manganese dioxide with chloroform gave no sulphone. The oxidation would appear to be complete, as in the analogous case of thiophen.[27]

Bromination of the three Thiophthen Preparations.

Solid Thiophthen.—The solid thiophthen, m. p. 56° (1 g.), in carbon disulphide was treated with excess of bromine in the same solvent, when much hydrogen bromide was evolved. After standing for 2 days the mixture was warmed for 20 minutes on the steam bath, excess bromine removed with strong potassium hydroxide, the solution washed with water and dried over calcium chloride. Removal of the solvent left a solid which crystallised from benzene in needles of constant m. p. 230–231°.

0·2253 g. gave 0·3969 g. AgBr; Br = 69·9.
0·2034 g. gave 0·2162 g. $BaSO_4$; S = 14·6.
$C_6S_2Br_4$ requires Br 70·1; S = 14·1 per cent.

The above compound of m. p. 230–231° was obtained when the crude product (S) was similarly brominated, thus confirming the presence of the solid

isomer (T) (see p. 139). An impure tribromothiophthen was also obtained from the reaction product.

Liquid Thiophthen (S_1).—0·5 g. of the oil was brominated as before. On removal of carbon disulphide the residue dissolved completely in alcohol, indicating the absence of the tetrabromo-derivative, m. p. 230–231°, and hence of (T) in the oil (S_1). The alcohol deposited a faintly pink microcrystalline solid of m. p. 121°, which, on recrystallisation from alcohol, was constant at 123–124°.

9·75 mgs. gave 14·705 mgs. AgBr; Br = 63·9.
9·575 mgs. gave 11·825 mgs. $BaSO_4$; S = 17·1.
$C_6HBr_3S_2$ requires Br = 63·6, S = 17·1 per cent.

Liquid Thiophthen (*C*).—0·5 g. was brominated in carbon disulphide as before, giving a clean white product of constant m. p. 123–123·5° after one crystallisation from alcohol. It did not depress the m. p. of the tribromo-derivative from S_1. On sublimation on the steam-bath fine silvery needles of m. p. 118° were obtained, which, however, on one recrystallisation from alcohol again melted at 123–124°. The change in m. p. may have been due to slight decomposition or a trace of impurity, but analysis of the product m. p. 118° agreed with the composition of a tribromothiophthen.

8·44 mgs. gave 10·695 mgs. $BaSO_4$; S = 17·4.
7·87 mgs. gave 11·695 mgs. AgBr; Br = 63·2.
$C_6HBr_3S_2$ requires S = 17·1, Br = 63·6 per cent.

Reduction of Solid Thiophthen with Sodium and Alcohol.

The thiophthen (m. p. 56°; 5 gs.) in absolute alcohol was heated under reflux and sodium (5 gs.) slowly added and heating continued till all had dissolved. The solvent was then removed, water added and the mixture extracted with light petroleum, b. p. 40–60°. The aqueous liquor was then acidified with hydrochloric acid, again extracted, and dried with calcium chloride.

The first extract yielded unchanged thiophthen, the second a yellow oil, b. p. 195–197°, with a very unpleasant odour. Its solution in alcohol was boiled with excess of yellow mercuric oxide and filtered hot. On cooling yellow needles, m. p. 75–76°, were deposited which underwent slight decomposition with more hot alcohol and were recrystallised from light petroleum, b. p. 40–60°. An analysis was performed by decomposing with cold hydrochloric acid (1 : 1), diluting with water to 200 c.c. and passing hydrogen sulphide.

0·2206 g. gave 0·1036 g. HgS; Hg = 40·5.
0·1040 g. gave 0·0497 g. HgS; Hg = 41·2.
$(C_6H_7S_2)_2Hg$ requires Hg = 41·2 per cent.

Nitration of the Isomeric Thiophthens.

Solid Thiophthen (*T*).—2·4 gs. were dissolved in the minimum quantity of acetic anhydride at about −10°. The mixture was cooled in ice and salt, well stirred, and 2 c.c. of a solution prepared from 3 c.c. nitric acid (d. 1·52) and 10 c.c. acetic anhydride slowly added. The mixture was left for 2

hours and then poured into ice water containing excess of sodium bicarbonate and distilled in steam. About 0·5 g. of partially nitrated thiophthen first came over and then 1·6 gs. of yellow nitro-compound (70 per cent. yield). This was boiled with animal charcoal in excess alcohol, filtered and diluted with water. Yellow needles of m. p. 124·5–125°, unchanged on recrystallisation from alcohol, were obtained. It is of some interest that a mixture of this nitro-compound with that obtained from the liquid thiophthen (S_2) m. p. 125·5–126° melted at 124·5–126°. There is, therefore, no depression of m. p. even in the case of these two obviously different compounds.

4·786 mgs. gave 6·835 mgs. CO_2 and 0·760 mg. H_2O; C = 38·95, H = 1·77.
8·328 mgs. gave 20·880 mgs. $BaSO_4$; S = 34·47.
2·701 mgs. gave 0·178 c.c. N_2 at 24° and 757 mm.; N = 7·53.
$C_6H_3O_2NS_2$ requires C = 38·9; H = 1·62; N = 7·6; S = 34·65 per cent.

Liquid Thiophthen (*C*).—2 gs. were nitrated as already described for (T). Steam distillation gave about 1 g. of a partly nitrated mixture and then 0·5 g. of nitro-compound, which was purified as before, giving lemon-yellow needles from alcohol of constant m. p. 122–123°.

4·890 mgs. gave 6·98 mgs. CO_2 and 0·73 mg. H_2O; C = 38·93, H = 1·67.
12·04 mgs. gave 30·35 mgs. $BaSO_4$; S = 34·65.
$C_6H_3O_2NS_2$ requires C = 38·9, H = 1·62, S = 34·65 per cent.

Liquid Thiophthen (S_2).—2·4 gs. were nitrated as before, using 2·4 c.c. of the solution employed for (T). The reaction mixture was cooled in ice and salt throughout and 0·7 g. of partially nitrated product and 0·5 g. (30 per cent.) of nitro-compound were obtained, m. p. 125·5–126°, unchanged on recrystallisation from alcohol.

4·730 mgs. gave 6·740 mgs. CO_2 and 0·700 mg. H_2O; C = 38·86, H = 1·65.
2·974 mgs. gave 0·194 c.c. N_2 at 24° and 757 mm.; N = 7·46.
9·888 mgs. gave 24·860 mgs. $BaSO_4$; S = 34·6.
$C_6H_3O_2NS_2$ requires C = 38·9, H = 1·62, N = 7·6, S = 34·65 per cent.

The nitro-compound gave no picrate nor did it react with aqueous mercuric chloride.

All the three nitro-compounds just described could be sublimed on the steam bath unchanged in m. p.

Reduction of the Nitro-compound from Thiophthen (S_2).—The reduction was carried out with stannous chloride according to the method of Fries and Hemmecker.[28] 3·6 gs. of the nitro-compound, m. p. 125·5–126°, were treated with 11·5 c.c. of alcohol and 76·5 c.c. of stannous chloride in hydrochloric acid (1 c.c. = 0·16 g. Sn). On standing overnight a yellow crystalline double compound of the amine with stannic chloride had separated (1·8 gs.). This solid was decomposed with sodium hydroxide under ether, the ether extract separated, excess acetic anhydride added and the ether removed on the steam bath. Excess sodium bicarbonate solution was added to decompose the acetic anhydride, and the yellow solid now remaining recrystallised from water and then from benzene, when the acetyl

aminothiophthen was obtained in the form of colourless silky needles of constant m. p. 220·5–221·5°. A further quantity of base was obtained from the tin chloride liquors and acetylated as before.

9·018 mgs. gave 21·140 mgs. $BaSO_4$; S = 32·2.
0·281 and 0·327 mg. in 3·140 and 4·470 mgs. camphor gave depressions of 17·9° and 14·8°. Mol. Wt. = 200, 198.
$C_8H_7ONS_2$ requires S = 32·5 per cent. Mol. Wt. = 197.

Preparation of the Methyl Ketones from the Isomeric Thiophthens.

Liquid Thiophthen (S_2).—The thiophthen (2·1 gs.) and acetyl chloride (2 gs.) in carbon disulphide (20 c.c.) were gradually added to a solution of anhydrous stannic chloride (4 gs.) in carbon disulphide (20 c.c.). The mixture immediately became green and a dark-coloured solid separated. The whole was allowed to stand for 2 hours, warmed to 50° for half an hour and then allowed to stand overnight. On adding ice-water, the solid disappeared and the orange-coloured carbon disulphide layer was separated, washed with water, dried over potassium carbonate and evaporated. The dark brown residue was boiled with animal charcoal in alcohol. The hot filtrate was diluted with water and on cooling deposited silvery plates, m. p. 107–108° (2·1 gs.; 90 per cent. yield). Recrystallisation from alcohol gave a product of constant m. p. 113° which depressed the m. p. of the ketone (m. p. 126–127°) from (T) (see below) to 104–105°.

4·794 mgs. gave 9·230 mgs. CO_2 and 1·410 mgs. H_2O; C = 52·5, H = 3·3.
10·279 mgs. gave 26·30 mgs. $BaSO_4$; S = 35·2.
$C_8H_6OS_2$ requires C = 52·7; H = 3·3; S = 35·2 per cent.

The alcoholic mother-liquors yielded fractions of m. p.'s ranging from 89° to 107°. It appeared possible that sublimation might purify these crude specimens and at the same time allow of a separation of the ketone derived from the small amount of impurity adhering so tenaciously to liquid thiophthen (see p. 144). Sublimation on the steam bath of a specimen of m. p. 107–108° gave beautiful needles, m. p. 109–110°, and no separation could be effected.

The 2 : 4-dinitrophenylhydrazone was prepared from the pure ketone, m. p. 113°, as in the case of the derivative from solid thiophthen; it melted at 267–268° after recrystallisation from ethyl acetate. In admixture with the latter (m. p. 267–268°) depression to 260° took place.

Reduction of the ketone, m. p. 113°, to the ethylthiophthen was effected thus:—

6 gs. of amalgamated zinc wool (see below) were added to 0·8 g. of the ketone and heated with 50 c.c. dilute hydrochloric acid (1 : 1) for 25 hours. Extraction with ether and fractionation gave 0·4 g. of an oil, b. p. 120–125° at 15 mm.

4·959 mgs. gave 10·42 mgs. CO_2 and 2·26 mgs. H_2O; C = 57·3, H = 5·0.
13·108 mgs. gave 36·175 mgs. $BaSO_4$; S = 37·9.
$C_8H_8S_2$ requires C = 57·1, H = 4·8, S = 38·1 per cent.

This ethylthiophthen gave a picrate, m. p. 70°, which was very soluble in methyl alcohol.

Liquid Thiophthen (*C*).—Thiophthen (0·8 g.) and acetyl chloride (1 g.) in carbon disulphide (10 c.c.) were slowly run into a solution of anhydrous stannic chloride (2 gs.) in carbon disulphide, the mixture allowed to stand overnight and treated as before, giving 1 g. of silvery needles of m. p. 115–116° (yield 90 per cent.).

4·926 mgs. gave 9·530 mgs. CO_2 and 1·510 mgs. H_2O; C = 52·8, H = 3·4.
5·178 mgs. gave 13·201 mgs. $BaSO_4$; S = 35·0.
$C_8H_6OS_2$ requires C = 52·7, H = 3·3, S = 35·2 per cent.

The ketone (0·32 g.) in alcohol (6·5 c.c.) was boiled with hydroxylamine hydrochloride (0·24 g.) and barium carbonate (0·37 g.) for several hours. On filtration the hot liquid gave 0·2 g. of white crystals of constant m. p. 160–161°, consisting of *methylthiophthienyl oxime*.

7·829 mgs. gave 18·230 mgs. $BaSO_4$; S = 32·0.
0·413 and 0·267 mg. in 4·208 and 2·740 mgs. camphor gave depressions of 18·3° and 18·0°; Mol. Wt. = 211, 217.
$C_8H_7ONS_2$ requires S = 32·5 per cent.; Mol. Wt. = 197.

Solid Thiophthen (*T*).—The ketone was prepared by the method already described from acetyl chloride (3 gs.), thiophthen (4 gs.), stannic chloride (18 gs.) in 100 c.c. carbon disulphide. The yield was 4 gs. (80 per cent.) of short needles of m. p. 124°, raised to 126–127° on recrystallisation from alcohol.

4·881 mgs. gave 9·39 mgs. CO_2 and 1·54 mgs. H_2O; C = 52·5, H = 3·8.
13·44 mgs. gave 34·135 mgs. $BaSO_4$; S = 35·2.
$C_8H_6OS_2$ requires C = 52·7, H = 3·3, S = 35·2 per cent.

The oxime of this ketone was prepared as in the previous case and crystallised from alcohol, m. p. 172–173°.

2·876 mgs. gave 0·176 c.c. N_2 at 23° and 747 mm.; N = 6·9.
12·139 mgs. gave 28·470 mgs. $BaSO_4$; S = 32·2.
$C_8H_7ONS_2$ requires N = 7·1; S = 32·5 per cent.

A small quantity of the ketone (from solid thiophthen) in alcohol was added to a solution of 2 : 4-dinitrophenylhydrazine in the minimum amount of concentrated sulphuric acid. The dark red precipitate was recrystallised from ethyl acetate, m. p. 267°.

6·657 mgs. gave 8·465 mgs. $BaSO_4$; S = 17·5.
$C_{14}H_{10}O_4N_4S_2$ requires S = 17·7 per cent.

The reduction to the corresponding ethylthiophthen was effected by heating 25 gs. of amalgamated zinc wool (prepared by immersion of the zinc wool in 3 per cent. aqueous mercuric chloride for 10 minutes), 150 c.c. hydrochloric acid (1 : 1) and 4 gs. of the ketone for 12 hours under reflux. The resulting oil on fractionation frothed and partly solidified. Ether then left a brown solid undissolved which could not be identified. The ether extract gave an oil (0·5 g.), b. p. 120° at 15 mm.

4·993 mgs. gave 10·35 mgs. CO_2 and 2·15 mgs. H_2O; C = 56·5, H = 4·8.
11·616 mgs. gave 32·84 mgs. $BaSO_4$; S = 38·8.
$C_8H_8S_2$ requires C = 57·1, H = 4·8, S = 38·1 per cent.

Though the result for carbon is low the analysis clearly shows that the product is an ethylthiophthen. It formed an orange picrate the quantity of which was insufficient for more than one recrystallisation. It then melted at 65° and was very soluble in methyl alcohol. Its properties clearly indicated, however, that it could not constitute the impurity present in the picrate of the thiophthen (S_2) (see p. 137).

Attempted Preparation of α-Thienyl Mercaptan. Isolation of Dithienyl Sulphide.

Taboury [29] obtained phenyl mercaptan and diphenyl disulphide from the action of sulphur on magnesium phenyl bromide. It was hoped to obtain α-thienyl mercaptan, $C_4H_3S{\cdot}SH$, by an analogous reaction and to use it for the synthesis of thiophthen (C).

To a cooled ethereal solution prepared from α-bromothiophen (10 gs.) and magnesium (1·5 gs.) in ether (120 c.c.) precipitated sulphur (4 gs.) was slowly added. No reaction occurred at 0°, so the mixture was gently boiled for 2 hours and left overnight. The mixture was cooled to − 15° and 2*N*-hydrochloric acid (100 c.c.) slowly added. Some hydrogen sulphide was evolved and much unchanged sulphur separated. The ether layer was washed with water, evaporated, and the residual oil distilled in steam. A small amount was volatile, but the bulk remained behind. Neither portion had an odour of mercaptan. The residue was fractionated, when a yellow oil of b. p. 155° at 14·5 mm. was obtained. This did not solidify in a freezing mixture. From its b. p. it appeared to be dithienyl sulphide, as will be seen from the following table of the b. p. and m. p. of analogous phenyl and thienyl derivatives.

Phenyl mercaptan, b. p. 172–175°. Thienyl mercaptan, b. p. 166°.
Diphenyl disulphide, m. p. 60–61°. Dithienyl disulphide, m. p. 55–56°.
Diphenyl sulphide, b. p. 157° at 16 mm.

Oxidation to Dithienyl Sulphone.—About 0·5 c.c. of the oil was dissolved in glacial acetic acid and excess of "perhydrol" added. After 2 days a white precipitate was obtained on pouring into water. On recrystallisation from alcohol this had m. p. 130–131°.

4·860 mgs. gave 7·52 mgs. CO_2 and 1·31 H_2O; C = 42·1; H = 3·0.
11·839 mgs. gave 36·08 mgs. $BaSO_4$; S = 41·9.
$C_8H_6O_2S_2$ requires C = 41·8; H, 2·6; S = 41·8 per cent.

The authors are greatly indebted to Mr. Cyril Marsden, B.Sc., who collaborated in the early stages of this work, and who isolated the first specimens of solid thiophthen and the corresponding picrate. He also first observed the formation of the picrate, m. p. 139–141°, formed from the mixture of the two thiophthens (S) and (T).

Messrs. J. L. Stoves, B.Sc., and F. H. Dews, B.Sc., rendered valuable assistance in the preparation of material.

The micro-analyses recorded in this communication were performed by Dr. A. Schoeller of Berlin.

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COLD TEST FOR FUELS.*

By B. H. Moerbeek (Member) and A. C. van Beest.

SUMMARY.

The authors expound the objections which can be raised against the present methods of pour-point determination for fuels, especially the A.S.T.M. method.

Their experiments have convinced them that the difficulty is due to the presence of asphaltenes in most residual fuels, which asphaltenes influence the mode of crystallisation of the paraffin wax. This influence differs with the temperature of pre-treatment.

An explanation is given of this effect of the asphaltenes, and a method for determining the pour point is proposed, which gives better correlation with the behaviour of fuels in practice than the present methods.

Introduction.

It may be considered a well-known fact that the A.S.T.M. pour-point test in its present form affords inadequate indications as to the anticipated behaviour of fuels at lower temperature.

Dissatisfaction with the A.S.T.M. pour-point test is sufficiently evident from the A.S.T.M. symposium on Motor Lubricants,[1] while Moore and Beard [2] even go so far as to doubt whether a really good test will ever be found. They say:

"The above work . . . points to the improbability of developing a method which will be universally applicable to all oils."

The objections to the A.S.T.M. pour-point test may be summed up as follows:

First, in many cases the pour point is dependent on the temperature at which the sample is pre-treated, and on the thermal history † of the batch from which it has been taken.‡ This may often upset reproducibility because waiting for 24 hours before testing (as prescribed by A.S.T.M. D 97–33) does not give any guarantee for the total elimination of the influence of the thermal history; moreover, in actual practice it is often impossible to wait 24 hours before testing. Furthermore, this sensitivity to temperature results in a minimum and a maximum pour point, which may lie very far apart, and thus be very confusing to the consumer. The consumer will be inclined to consider the A.S.T.M. maximum pour point as being the one he is most interested in, as giving the highest guarantee against trouble. There can, however, be no doubt that in most cases, if not in all, the temperature at which the fuel may still be used without difficulty is considerably lower than the maximum pour point. (For

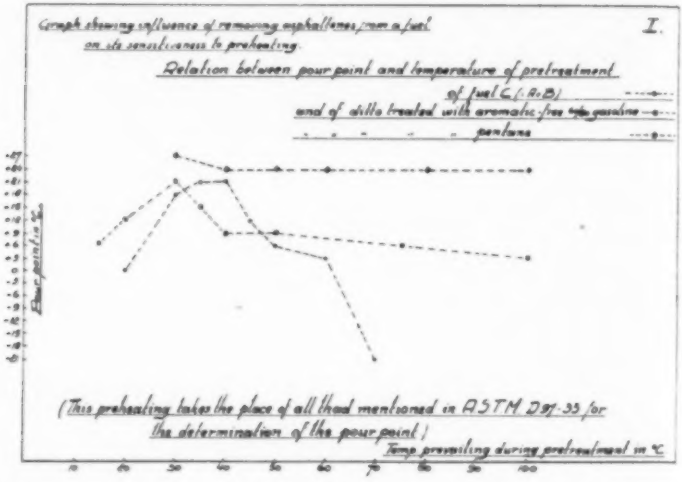
* Paper presented for discussion at the One Hundred and Sixty-Second Meeting of the Institution of Petroleum Technologists, January 8th, 1935.

† By thermal history is meant the fluctuations of temperature to which the sample has been subjected during its whole life.

‡ Only the true pour point of wax-containing fuels is dealt with, not the apparent pour point which is found on the increase of viscosity at low temperature in the case of non-waxy fuels.

fuel D, graph IV, for instance, it has been proved in practice that at + 5° C. one can still use it, whilst the maximum pour point is + 27° C. Besides, the A.S.T.M. maximum pour point is not by any means always the true maximum pour point.) (See graph I.) This is also known from the literature on the subject.[3] The indications given in this report of the A.S.T.M. sub-committee[3] for finding the "true maximum pour point" are omitted in the A.S.T.M. prescription D 97–33.

The primary purpose of the investigation described in this paper was: (A) to discover why some oils with respect to their pour points are sensitive


Graph showing influence of removing asphaltenes from a fuel on its sensitiveness to preheating.
I.
Relation between pour point and temperature of pretreatment
of fuel C (i.e. B)
and of oil to treated with aromatic free petroleum ether
pentane
Pour point in °C.
(This preheating takes the place of all those mentioned in A.S.T.M. D97-33 for the determination of the pour point.)
Temp. prevailing during preheatment in °C.

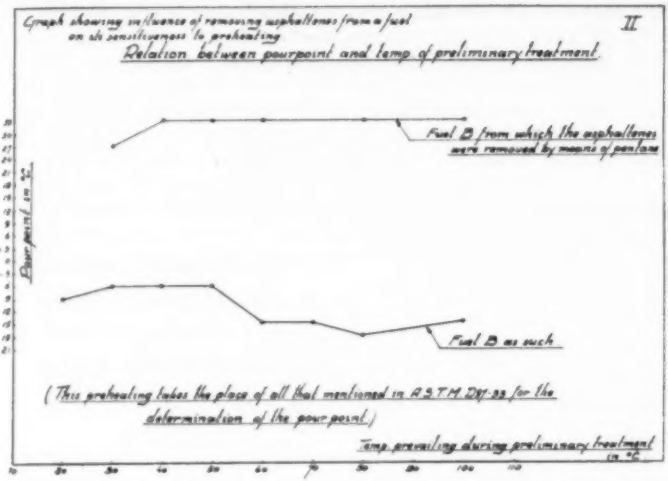
to their thermal history, and (B) to find a method, the results of which should, if possible, be independent of these factors, at the same time corresponding better to the temperature at which the fuel still renders adequate service in practice.

Although we have as yet insufficient data to prove that we have completely succeeded, we think that a useful purpose will be served by publishing our results now, in order to stimulate interest and to evoke criticism and discussion.

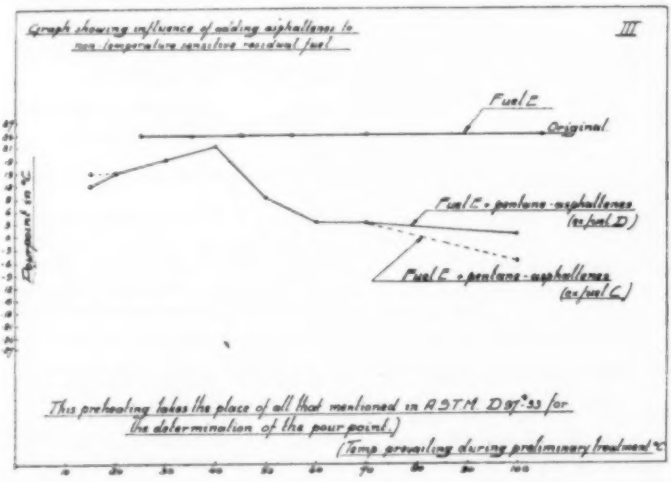
A. Present Pour-Point Determinations and the Cause of their Inadequacy.

I. It is a well-known fact that distillate fuels are not temperature sensitive with respect to their A.S.T.M. pour point. On the other hand, residual fuels very often give different results when pre-heated to different temperatures. It was surmised by the authors that the asphaltenes present in residual fuels had something to do with their sensitiveness to their thermal history. To elucidate this point, a small percentage of asphaltenes precipitated with pentane from residual fuels was added to a residual fuel (fuel E in graph III), the pour point of which was insensitive to the

temperature of pre-treatment. These asphaltenes were obtained by dissolving a fuel containing them in a tenfold quantity of pentane, then


Graph showing influence of removing asphaltenes from a fuel on its sensitiveness to preheating
II
Relation between pourpoint and temp of preliminary treatment
Fuel B from which the asphaltenes were removed by means of pentane
Fuel B as such
Pourpoint in °C
(This preheating takes the place of all that mentioned in A.S.T.M. Dif.-33 for the determination of the pour point)
Temp prevailing during preliminary treatment in °C

leaving it overnight and separating the precipitated asphaltenes. The precipitates, while still in a wet state, were rubbed fine in a mortar and dissolved in fuel E.


Graph showing influence of adding asphaltenes to non-temperature sensitive residual fuel
III
Fuel E
Original
Fuel E + pentane-asphaltenes (ex fuel D)
Fuel E + pentane-asphaltenes (ex fuel C)
Pourpoint in °C
This preheating takes the place of all that mentioned in A.S.T.M. Dif.-33 for the determination of the pour point.)
(Temp prevailing during preliminary treatment °C

As will be seen from graph III, the pour point has now become sensitive to the temperature of pre-treatment.

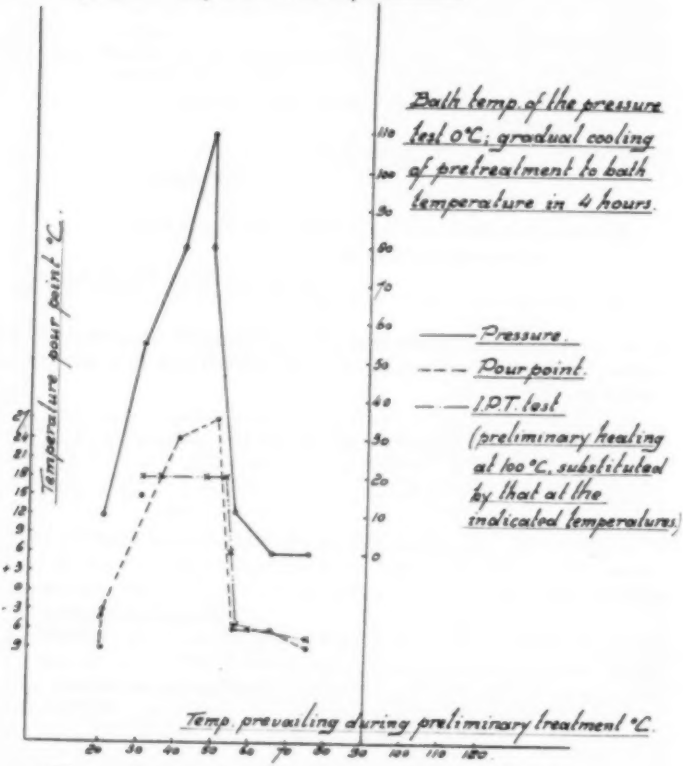
On the other hand, a fuel which in itself is temperature sensitive as to its pour point can be made insensitive by removing the asphaltenes by

pentane. This is proved by graphs I and II, which show very clearly the result of the removal of the asphaltenes.

The removal of the substances which make the fuel temperature sensitive

IV

Relation between pour point, pressure measured in pressure apparatus[1] and temp. prevailing during preliminary treatment of Fuel D.


Bath temp. of the pressure test 0°C; gradual cooling of pretreatment to bath temperature in 4 hours.
Pressure.
Pour point.
I.P.T. test
(preliminary heating at 100°C. substituted by that at the indicated temperatures)
Temperature pour point °C.
Temp. prevailing during preliminary treatment °C.

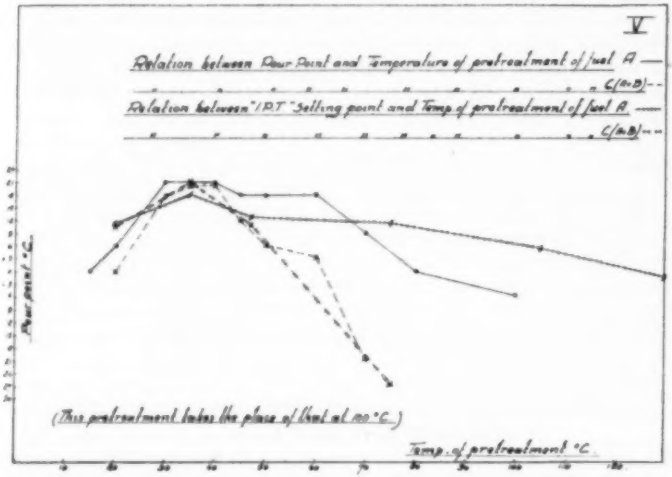
(This preheating takes the place of all that mentioned in A.S.T.M. D97-33 for the determination of the pour point)

[1] Described in text II 6.

can be brought about by other means than by extraction with pentane. For instance, fuel D (graph IV), a fuel particularly sensitive to the temperature of pre-treatment, after being refined with 2 per cent. of sulphuric acid and 20 per cent. of terrana earth at about 80° C., has become completely immune to changes in temperature of pre-treatment. Some fuels can be

made immune even by refining with 20 per cent. of terrana only. Such a treatment does away with an objection which might be raised when precipitating the asphaltenes with pentane; namely, that a slight trace of high-melting paraffin wax (petroleum ceresin) might be removed, thereby altering the pour point. The treatment to which fuel D (graph IV) has been subjected can hardly have removed high-melting paraffin wax, and yet the fuel has become immune to temperature changes. That removal of high-melting wax is not the cause of the phenomenon is further supported by the fact that the addition of petroleum ceresin to a temperature-insensitive fuel (E) has no influence at all on its sensitivity.

A phenomenon which complicates the finding of an unassailable pour-point determination is that a fuel may for a long time "remember" the temperature to which it has been raised at some given period.


V
Relation between Pour Point and Temperature of pretreatment of fuel A
Relation between "I.B.T." Boiling point and Temp. of pretreatment of fuel A
Pour point °C.
(This pretreatment takes the place of that at 100 °C.)
Temp. of pretreatment °C.

II. From graphs I to VI it is clear that the behaviour of a temperature-sensitive fuel is really determined by a curve. The curve formed by the pour points determined after pre-treatments at different temperatures does not give sufficient indication of the minimum temperature at which the fuel can be used. The maximum point of the curve is certainly much too high, and the minimum point definitely too low. Apart from this, the A.S.T.M. maximum does not always represent the true maximum pour point (see graphs I and II).

It is known from practical experience that fuels are often, if not always, freely flowing at temperatures of 15–20° C. below their A.S.T.M. maximum pour point. This discrepancy between the test and actual practice may be due to various causes, viz.:

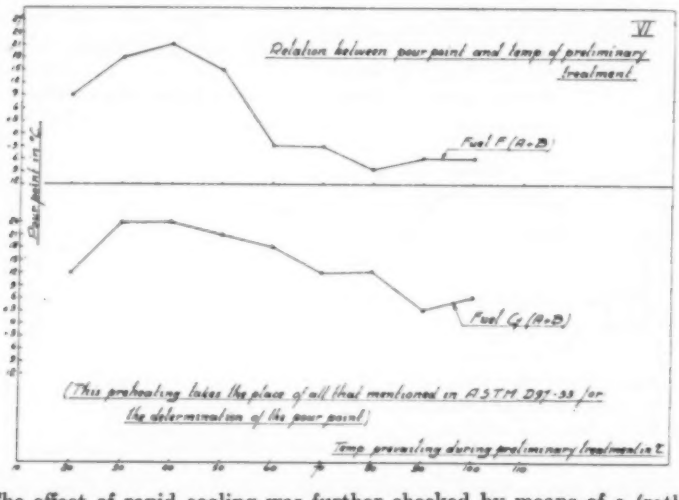
(*a*) To the thermal sensitiveness of the fuel, notably after-effects of the high temperature to which it has been subjected in operation. The investigation has shown that above a certain temperature of pre-treatment, which in many cases lies near the A.S.T.M. temperature of pre-treatment,

it may be said that the higher this temperature, the lower the pour point (graphs I–VI).

(*b*) A second defect in the A.S.T.M. pour-point determination is the rapid cooling (ref. 1, p. 45). Some fuels thereby show higher pour points than with gradual cooling, whilst it may be assumed that in actual practice a fuel is only subjected to slow cooling.

The following figures prove this. A Rumanian waxy fuel was first cooled so rapidly that the difference in temperature between the oil and the cooling bath remained about 10° C. down to the pour-point temperature; secondly, the same fuel was cooled with a difference of 1–3° C. between the bath and the oil. In the first case the A.S.T.M. pour point was + 23° C., in the second + 14° C.

Another fuel (D of graph IV), treated in the same way, showed + 27° and + 8° C., respectively.


VI
Relation between pour point and temp of preliminary treatment
Pour point in °C.
Fuel F (A+B)
Fuel G (A+B)
(This preheating takes the place of all that mentioned in A.S.T.M. D97-33 for the determination of the pour point)
Temp prevailing during preliminary treatment in °C

The effect of rapid cooling was further checked by means of a (rather primitive) flow test. Some oils, hereafter indicated by m_1, m_2, and m_3, were cooled in a ½-inch iron tube about a yard long, while the pressure required to put the liquid into motion was determined; the results were as follows:

	a. iron tube with the oil, heated to 35° C., then immediately placed in a bath at 0° C.	*b*. duplicate of (*a*) heated to 35° C., then very gradually cooled in 5 hours to 0° C.
A.S.T.M. p.p. + 6° C.;	pressure required to put the liquid into motion > 1 atm.	pressure = 6 cm. of mercury.
„ „ + 12° C.	do.	do. „ 13 „ „ „
„ „ + 18° C.		„ 37 „ „ „

(*c*) A further difference from practical circumstances is that in the A.S.T.M. pour-point determination stirring is carefully avoided; in

practice a fuel is always liable to be stirred or brought into motion by pumping and so on.

III. It might be supposed that the difficulty could be avoided by determining the minimum pour point. This is, indeed, what the I.P.T. setting point test (I.P.T. Standard Methods) attempts by specifying a very high temperature of pre-treatment, and indeed, by this means a determination is obtained which is practically independent of the thermal history of the sample. The reverse of the picture is, however, that the stipulated temperature of 100° C. is so high that the figures found are too low when compared with the behaviour in actual practice. Apart from this, even a pre-heating to 100° C. does not always guarantee a minimum pour point (see fuel C of graph V).*

IV. The most plausible explanation of the above-mentioned action of the asphaltenes is that on cooling from a sufficiently high temperature they become concentrated on the surface of the crystals. This impedes the formation of large crystals (*not of aggregates*), but the chief result of this "skin" of asphaltenes is that the paraffin-wax crystals retain much less oil, and cannot form a network of crystals so easily, which reduces the pour point. The asphaltenes, moreover, seem somewhat to retard the process of crystallisation.

There is an artifice by means of which one can remove the asphaltenes from the paraffin wax and thus rule out their effect on the pour point. This is by cooling from 100° C. to 0° C. and then heating to about 35° C. and again cooling. One thus, indeed, achieves the object in view; at 35° C. the main mass of the wax crystals has already dissolved, whilst the "skins" of asphaltenes from which the paraffin wax has been largely or wholly eliminated are obviously left behind in a state in which they cannot be "picked up" by the crystals separating out during the second cooling.

Hence, this is a device by means of which one can make the pour-point determination independent of the presence of asphaltenes; some manipulation of this kind was at one time suggested by the A.S.T.M. sub-committee ([3], p. 468), but was not included in A.S.T.M. D 97–33.

The great difference between the mode of crystallisation of the paraffin-wax crystals in a fuel containing asphaltenes (fuel D) on cooling to 20° C. after pre-heating to 100° C. and in the same fuel after the pre-treatment 100° C.–0° C.–35° C.–20° C. is sufficiently apparent from the photomicrographs A and B.

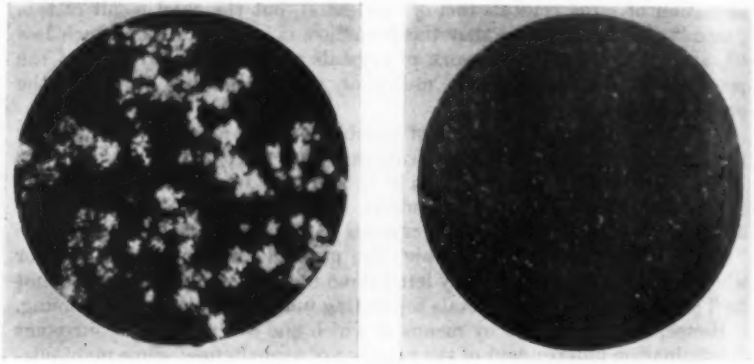
In A there are sharply defined crystal aggregates which stand out clearly against the oil, in B there is a gelatinous mass. Under the microscope it is also noticeable that the oil in A is disturbed much less in its free movement by the large crystal aggregates than that in B, although both have the same temperature.

These photos agree not only with the observations of Moore and Beard,[2] but also with the aspect of a paraffin wax-containing oil to which a special pour-point reducer, *e.g.* heated Dubb's residue, has been added. It is a known fact that asphaltenes are the active constituent of such a residue. From the above experiments it had appeared that sensitiveness to temperature in the pour-point determination was caused by asphaltenes, and

* A cold test, which, in the authors' opinion, avoids the disadvantages as well of the A.S.T.M. as of the I.P.T. method, is discussed under B hereafter.

so it was only natural to assume that the asphaltenes serve as pour-point reducers here, thus causing the symptom of sensitiveness to temperature. Zimmer, Davis, and Frohlich [4] have suggested that the pour-point reducer Paraflow is preferentially adsorbed by the wax, reducing the size of the larger crystals and preventing the adsorption of larger quantities of oil by the wax. A similar process is reported by Gurwitsch.[5] It must be observed here that Paraflow, and also other pour-point reducers, *e.g.*, the asphaltenes from Dubb's residue, have the same effect, viz., they further the formation of crystal aggregates. According to the literature on the subject, aggregation of crystals very often occurs in the presence of certain contaminants, especially if these are colloidal.[6]

In order to demonstrate that, in this case too, the pour-point reducer (viz. the asphaltenes) must be concentrated on the crystals to be active, the following experiments were made.



A B

1. Fuel D contained 2·8 per cent. by weight of pentane asphaltenes. It was heated to 75° C., cooled to 20° C., and filtered at 20° C. Filtration proceeded very quickly. The filtrate contained 1·5 (duplicate 1·8) per cent. by weight of pentane asphaltenes. The same fuel, having been pre-heated to 75° C., was cooled to 0° C., reheated to 30° C., then cooled again to 20° C. Filtration at 20° C. was now very slow, and the filtrate contained 3·1 (duplicate 2·8) per cent. by weight of pentane asphaltenes.

2. This same experiment was repeated with fuel C.

(*a*) The oil is heated to 75° C., cooled to 10° C., without any intermediate operations, and filtered at that temperature. Filtration proceeds quickly.

(*b*) The same oil was heated to 75° C., cooled to 0° C., then heated again to 30° C., cooled to + 10° C., and filtered at that temperature. Filtration is slow.

Asphaltenes in the filter oil of test *a*: 1·1 per cent.
" " " " " *b*: 2·0 "

Our explanation of this difference in filtration velocity and content of asphaltenes in the filter oil is, that in direct cooling from 75° C. to 10° or 20° C. the solubility of the asphaltenes in the oil quickly decreases, and they concentrate on the surface of the paraffin-wax crystals, and hence act as a pour-point reducer. On being heated from 10° or 20° C. to 30° or 40° C. a considerable portion of the wax crystals dissolves, whereas the "skins" of asphaltenes which covered the crystals remain at that temperature obviously in a condition in which they are not easily "picked up" again by the new crystals when cooling is restarted. Then the asphaltenes do not act as pour-point reducers, and are left in the filtrate.

A similar experiment was carried out with the apparatus described in II, *b* (see also graph IV), with a similar result.

1. Heated to . . .	100° C.						
2. In at least 2½ hours, cooled from 100° C. to . . .	30° C.	40° C.	30° C.	20° C.	20° C.	15° C.	15° C.
3. Heated to or kept at	40	40	30	35	20	35	15
4. Then gradually cooled to 0° C. maintained at 0° C. for 1 hour and shifting pressure determined	1 cm. mercury			20 cm. merc.	3 cm. merc.	60 cm. 40 cm. merc.	2 cm. 4 cm.

This table shows that the cooling of this fuel to 15° C. and its reheating to 35° C., followed by cooling to 0° C., practically eliminates the effect of the asphaltenes; cooling from 100° C. to 15° C., keeping it at that temperature, and afterwards cooling to 0° C. does not eliminate this effect.

Further experiments have enabled us to assume that the asphaltenes not only insulate the crystals from the oil, but that there is the possibility that they slightly retard the crystallisation. To find out this the authors determined the specific gravity of fuel C (either pre-heated or not) by means of a dilatometer.

Temperature at which the samples were kept: 20° *C.*

After	Fuel C, pre-heated/95° C.	Fuel C not heated.
1 day	0·9294 20/4° C.	0·9344
2 days	0·9293	0·9346
4 days	0·9294	0·9345
1 week	0·9298	(0·9351)
1 month	0·9305	0·9345
About 3 months	0·9305	0·9345
„ 4 „	0·9309	

The pre-heated fuel has a lower specific gravity than the non-pre-heated, which points to the presence in the first fuel of paraffin wax in solution, which, in the second fuel, has already crystallised out; the gradual increase in the specific gravity is indicative of the steady crystallisation of the paraffin wax. This happens very slowly, however; continuing at this rate it would take 8 months for the pre-treated fuel to catch up with the other.

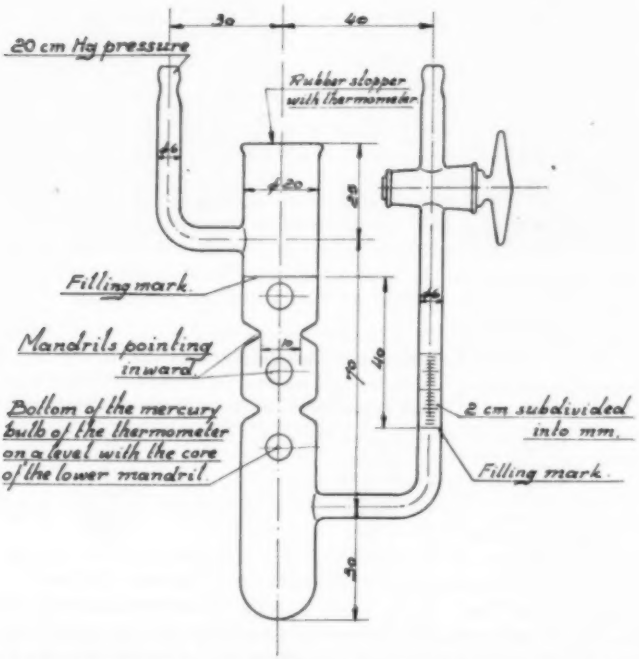
This single observation, however, is not in agreement with what the authors have hitherto found—namely, that a pour-point reducer influences, not the quantity of the crystallised paraffin wax, but only the nature of the crystallisation. They therefore regard it as an indication of the possibility—though not yet as a proof—that retardation of crystallisation to some extent also plays a part. In any case, this retardation, too, is caused by the asphaltenes.

B. Proposal for a Modified Cold Test which Avoids the Disadvantages of the Present Pour-Point Determinations.

According to the foregoing (IV), the objections raised to the pour-point determinations may be primarily met by excluding the influence of the

APPARATUS FOR FLOW TEST.

(The notches serve to prevent the oil sample from slipping down when the outer layer has already melted but the oil is still present in the tube in the form of a solid lump.)

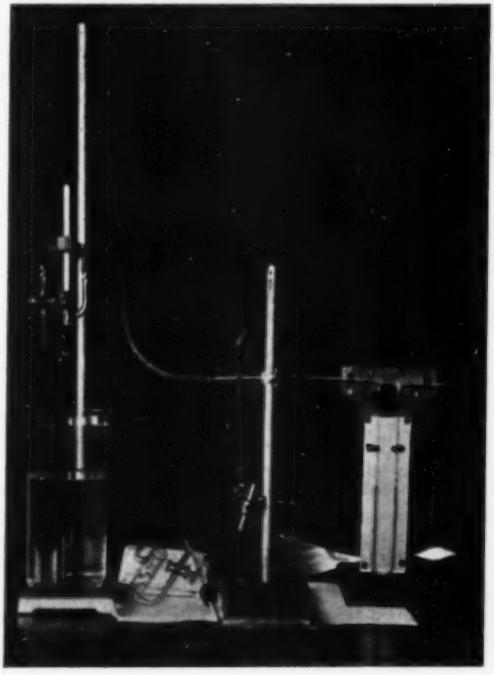


natural pour-point reducers (asphaltenes) on the determination. This may best be done by applying the expedient described above—namely, cooling to 0° C., heating to a temperature in the neighbourhood of 35° C., and only

subsequently cooling down for the actual pour-point determination. Better check values are obtained in this way than by the present method, and the maximum pour point is then certainly found. The drawback, however, that this maximum pour point is an under-statement, as it were, of the performance of the fuel in practice, continues to exist.

To remove this objection, we have devised the following tentative method, which, it would seem to us, reflects working conditions.

The guiding criterion of this method is, instead of the conventional pour point, the temperature at which the fuel can be shifted under a certain



pressure in a tube. Care has been taken that the fuel shall not move through "slipping," that is to say, it does not begin to move when the outermost layer has melted, but only when the network of crystals has disappeared from the entire liquid.

We have checked temperatures so obtained by the known minimum temperature at which the same fuel can still be used in actual practice.

We have taken 20 cm. of mercury as a pressure which certainly would not be regarded as abnormal in practice,* whilst 0° C. was taken as the

* The most unfavourable circumstances to which a fuel can be subjected in practice are considered to be free flow through a tube from a tank placed on a platform at a reasonable level above ground.

lowest temperature necessary to crystallise out most of the wax and to separate out the asphaltenes sufficiently.*

Hence the fuel is introduced into the apparatus shown in the sketch up to the filling marks, cooled to 0° C., heated to 35° C., and thereupon gradually cooled by only cooling the bottom part of the apparatus in a cooling bath which has a temperature of about 10° C. lower than the anticipated flow point. Not until about 5° C. above the anticipated flow point has been reached is the apparatus wholly immersed in the bath. Once the oil has assumed the temperature of the bath, the apparatus is placed under 20 cm. mercury pressure. The temperature of the bath is now raised by about 1° C. per 3–4 minutes and the temperature of the oil at which it has moved over 2 mm. is noted.

To show the effect of cooling and pre-heating to various temperatures on the results, we give below a series of flow-point determinations.

1. *Fuel D.* .

Pre-treatment: Cooling to			heating to		Flow pt.
0° C.,			+ 30° C.		+ 2° C.
0° C.,			+ 30° C.		+ 3° C.
0° C.,			+ 35° C.		+ 2½° C.
0° C.,			+ 40° C.		+ 2° C.
0° C.,			+ 50° C.		+ 1° C.
− 10° C.,			+ 30° C.		+ 3° C.

2. *Fuel C.*

Cooling to		heating to		Flow point
0° C.,		+ 20° C.		− 12° C. (− 11° C.).
0° C.,		+ 30° C.		− 4½° C.
0° C.,		+ 40° C.		− 0° C.
0° C.,		+ 50° C.		− 11° C.
− 10° C.,		+ 30° C.		− 3½° C.
− 10° C.,		+ 40° C.		− 4° C.
− 10° C.,		+ 50° C.		− 11° C.
− 20° C.,		+ 30° C.		− 4° C.
− 20° C.,		+ 50° C.		− 11° C.

3. Sample which incidentally had been kept at 90° C. for 72 hours.

Pre-treatment.	Pour Point (A.S.T.M. D 97–33 modified by altering temperature of pre-treatment).
100° C.; − 0° C.; − 20° C.	+ 17° C.
30° C.	+ 23° C.
40° C.	+ 23° C.
46° C.	+ 23° C.
50° C.	+ 23° C.
60° C.	+ 26° C.
70° C.	− 7° C.
90° C.	− 16° C.

For this fuel the influence of the asphaltenes does not begin to take effect until a higher temperature is reached than with a normal oil of this type, presumably as a result of the change mentioned (owing to the above referred to heating for 72 hours).

1. Flow point (after pre-treatment 0 to + 35° C.) = 0° C. duplic 0° C.
2. „ „ („ „ 225 to 0 to + 35° C.) = − 2° duplic − 1° C.
3. „ „ („ „ 225 to 0 to + 35 to − 12 to + 35° C.) = + 1° C.

* It is not impossible that cases may be found in which a lower temperature than 0° is required. It has been verified that the same result is obtained by cooling normal fuels to − 10 or − 20° C.

It is very clearly seen, particularly in the case of fuel C, that the temperature of pre-treatment at which a maximum flow point is found lies between 30° and 40° C. Below this temperature the paraffin wax has not re-dissolved to a sufficient extent; at temperatures above 40° C. it seems that the asphaltenes begin to dissolve. In both cases a lower flow point is observed. Thus at different temperatures of pre-heating a curve is obtained similar to that of graphs I and VI, but on a lower level. The suggested method, like the A.S.T.M. method, aims at determining the maximum of this curve.

As compared with the A.S.T.M. method, the suggested method would seem to have the advantage of indicating a temperature at which the fuel, even after the most unfavourable preliminary history, is still serviceable under working conditions. Admittedly it will in many cases also be utilisable below this temperature, but there is always a possibility in practice of chance heating to the dangerous temperature range of 30–40° C., shortly before the oil is subjected to a low temperature. On the other hand, the drawback to the A.S.T.M. method—namely, that the maximum point is often much higher than the temperature at which the fuel is still utilisable—is avoided here.

Conclusions.

1. Some fuels, especially residual fuels, give a pour point dependent on the temperature of pre-treatment. To remove this difficulty the A.S.T.M. maximum pour-point determination prescribes a temperature of pre-treatment by which it is surmised a maximum pour point is found. The objections to be made are, first, that the A.S.T.M. pour point is not always the maximum, and, secondly, that in most, if not all, cases a fuel will be freely flowing at a much lower temperature than the A.S.T.M. pour point indicates.

On the other hand, the I.P.T. setting point aims at a minimum pour point, which is too low as compared with actual practice.

2. The cause of this dependency of the pour point of a fuel on its thermal history is the presence of asphaltenes. Removal of these asphaltenes makes a fuel temperature-insensible. An explanation of this effect of the asphaltenes is that they, on cooling, separate out on the surface of the wax crystals, thereby preventing the formation of a cohesive crystal structure in the fuel.

3. A new method of determination is proposed which, though also aiming at a maximum point of a curve, adapts itself better to practical results. For this purpose the influence of the asphaltenes on the crystallisation of the wax is eliminated by a suitable pre-cooling, followed by pre-heating to such a temperature that the asphaltenes do not dissolve again, whilst instead of the pour point the temperature at which the fuel can be shifted under a fixed pressure is taken as a criterion.

The authors wish to thank the Directors of the Bataafsche Petroleum Maatschappij for their permission to publish this paper, and those members of the staff of the Amsterdam Laboratory who have assisted them with helpful suggestions.

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[4] "The Effect of Paraflow on Wax Crystallisation and the Pour Point of Lubricating Oils," J. C. Zimmer, G. H. B. Davis, and P. K. Frolich, of Standard Oil Development Co. Third Petroleum and Natural Gas Conference, The Pennsylvania State College, page 56.
[5] *Scient. Princ. of Petr. Techn.*, L. Gurwitsch. Ed. 1932, page 550. "Chemical contamination with resinous and asphaltic substances also impedes the formation of large crystals, and the presence of colloid substances makes the growth of large crystals impossible; the colloids are adsorbed by the surface of the small crystals as these are formed, and prevent the further free play of the crystallising forces."
[6] Kohlschutter and I. Marti; *Helv. Chim. Acta.*, 1930, **13**, 937.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE One Hundred and Sixty-Second General Meeting of the Institution was held at the House of the Royal Society of Arts, John Street, London, W.C.2, on Tuesday, January 8th, 1935, Mr. T. DEWHURST, the President, occupying the Chair.

The following paper was presented :—

"SULPHUR COMPOUNDS OF TECHNICAL INTEREST. THE ISOMERIC THIOPHTHENS." *

By FREDERICK CHALLENGER and JACK BLATCHLEY HARRISON.

DISCUSSION.

The President expressed his appreciation of the extremely detailed and exact scientific research carried out by the Authors of the paper, the results of which would undoubtedly be of great value in the future. He was sure all members present admired the clarity of Professor Challenger's explanatory address. They would be gratified that the execution of such a valuable piece of research had been furthered by various grants from the Research Fund of the Institution.

Dr. A. E. Dunstan said that he had had the opportunity at various times of seeing a good deal of the work in progress at the University of Leeds, and suggested that such fundamental knowledge was of the utmost importance. It was rather a slur on the industry at large that so little had been done—as witness our ignorance of hydrocarbon chemistry in petroleum, in spite of the excellent survey of the many problems by Dr. B. T. Brooks. So many directions for research of this sort existed, and one must pay tribute to the far-sightedness of our American colleagues in the remarkable programmes in fundamental research which were being carried out in a number of American Universities. It was equally unfortunate that so little was being done in this country.

It was with great regret that one so often met the question—"What practical use can such research be?" A short time ago Professor Bragg, at the Royal Institution, in describing the work of Volta, said that the year 1800 in which it took place could very appropriately be substituted for a great number of the customary dates in the history books. The fundamental work of Volta, Faraday and Davy, and many other names that came to mind, had had the practical effect of instituting vast new industries, and it would be a rash man in face of all this who would deny the value of work of this sort. Consequently he hoped that Professor Challenger's example would be followed, and had no doubt that the Institution's Research Fund would always be available for such researches.

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* See pp. 135–154.

Coming to particulars, it was interesting to visualise how the five-ring thiophens and their derivatives come into being. Friedman's work is very suggestive, but one could not help thinking that these bodies were simplification products of far more complicated structures in the original bituminous material. In the case of petroleum distillates it was obvious that the sulphur compounds were derived from complexes in, for example, the asphaltic end of the crude, and it was of interest to note that Ruzicka * had prepared rings from 8 up to 34 carbon atoms, and had shown that the civet and musk perfumes are due to ring ketones of 17 and 16 carbon atoms respectively. He also gives space models for such complexes as *cyclo*tetradecane and *cyclo*octacosane. This throws some possible light on the occurrence of very complicated structures in our own raw material and foreshadows further fundamental work of the first importance.

Dr. F. B. Thole said that the research which had just been described was a model of how a difficult problem in organic chemistry should be tackled. Only those who had had to analyse and purify the components of a black tarry product could appreciate what a tedious and laborious process it was, and the isolation of the pure derivatives which had been accomplished by Professor Challenger and Dr. Harrison bore testimony to their skill and patience.

He was also very desirous of stressing the fundamental importance of pure research of this nature. At first glance many might consider the work to have no practical relationship to petroleum technology, but there were in this country enormous deposits of sulphurous oil shale, at present practically valueless, and until chemists had a thorough knowledge of the chemical nature of the sulphurous bodies in the shale oil, there was little hope of the discovery of practical methods for eliminating them, and thereby creating an important source of indigenous oil.

As regards the difficulty of distinguishing between the two liquid thiophthens, it was evident that the chemical derivatives were too similar in properties to afford a reliable method of discrimination, and he therefore looked forward with much interest to the application of various physical means for characterising these liquids. It was in this direction that success appeared to be most probable.

Mr. E. A. Evans said that the last two speakers had referred specifically to the academic side of the work. Dr. Thole had made reference to the shale oils which might be available if one only knew how to deal with the sulphur. But must we confine ourselves to problems of the future? Surely the present state of turbine oil is sufficient to centre our minds upon problems of the moment. Turbine users are definitely afraid to use oils with a sulphur content of more than 0·3 per cent. merely because there is so little knowledge about the sulphur compounds in the oil. After all, it may be perfectly safe to use an oil with 0·5 per cent. of sulphur, or even more, in a turbine if we were assured that we knew sufficient about the behaviour of the sulphur compounds present. We are just suffering from ignorance. Extreme pressure lubricants would be very much better understood and probably popularised if we knew a little

* *Chem. & Ind.*, 1935, **54**, 2.

more about the sulphur compounds. Any academic work, therefore, which was being done on the subject of sulphur had a very definite and immediate practical value.

Professor F. Challenger, in replying to the discussion, said he very much appreciated the remarks which had been made.

Dr. Dunstan had asked whether he could give any views on the nature of the sulphur compounds which existed in shale or in petroleum before distillation. There was no doubt that, in spite of all the work which had been done on the extraction of bituminous material with solvents, the various extracts merited a very much closer chemical investigation than any of them had received until recently, although at least twenty years had elapsed since coal had been first extracted with an organic solvent. Two papers recently published * showed that in a certain oil shale before distillation, in crude petroleum and in asphalt, porphyrin derivatives were contained. That definitely indicated the presence of extremely complex substances. The porphyrin substances were definitely derived from vegetable matter of the nature of chlorophyll and to a probably lesser extent from animal matter. These two papers were of the highest importance from the chemical, geological and botanical standpoints. This discovery was only rendered possible by the extensive earlier researches on the chemistry of chlorophyll and hæmoglobin carried out by many investigators from the academic standpoint.

He was sorry he could not be more explicit about the identity of the two liquid thiophthens, but he hoped to be able to present more complete results to the Institution before long. The present results of the research were not, however, being published prematurely, as he had been engaged on the work for three years.

In conclusion, he wished to express his great appreciation of the continued financial support given by the Institution to this research work.

On the proposition of **The President,** a hearty vote of thanks was accorded to Professor Challenger and Dr. Harrison for their interesting and valuable contribution.

The following paper was then read by Mr. Moerbeek :—

"COLD TEST FOR FUELS." †

By B. H. Moerbeek and A. C. Van Beest.

The President congratulated the Authors on the great clearness with which the main thesis of the paper had been presented, and also congratulated Mr. Moerbeek on having so successfully surmounted the language difficulty.

Mr. J. McConnell Sanders said that at the commencement of the paper the Authors dissociated the subject of it from the question of

* *Liebig's Annalen der Chemie,* 1934, **509,** 103; **510,** 42. † See pp. 155–168.

increase in viscosity in asphaltic fuel, and he would like to ask whether they would not be inclined to ascribe the phenomenon of increase of viscosity in the case of mixed base crudes to adsorption of asphaltenes by the wax crystals.

As a member of several Committees on standardization, he was inclined to reflect somewhat sadly that nothing seemed to be so unstable as a standard method. When a method had been made a standard, someone came along later with a new type of product which caused trouble with the set conditions of test, and the standard method then became useless. It had been found, of course, that cold tests, cloud tests, and pour tests were not easily reproducible, and as time went on, and products were produced by new commercial methods of refining, they seemed to become more and more susceptible to the peculiar influences of test conditions.

He was rather intrigued by the Authors' remark that fuel oil was capable of remembering its thermal history, and he would like to ask whether the Authors could give some idea of the length of a fuel oil's memory. How long could the fuel oil remember its thermal history! In other words, how long did one have to wait before it forgot its past and ceased to give consistently bad cold tests by the A.S.T.M. method?

He noticed that the Authors applied their remarks chiefly to fuel oils containing asphaltic products—in other words, residual fuel oils—but he thought that even in distillate oils there were similar phenomena. He noticed, for instance, that in the application of solvent extraction methods to lubricating oils, using a solvent such as trichlorethylene, the mere application of a solvent which was a better solvent for asphaltenes than for the waxy hydrocarbons present in the oil, resulted in a closer approximation of cloud and pour-point than in the case of an oil treated by the usual refining methods. Was not it possible that here again there was adsorption by the wax crystals of some substance analogous to asphaltenes which had come over in the distillate, being formed in the process of refining?

Mr. Brocades Zaalberg referred to the Authors' statement that in order to eliminate the influence of the asphaltenes on the crystallisation of the wax they heated the fuel to 100° C., then cooled it at a low temperature, then heated it again to about 35° C., after which the flow-point was determined; he asked whether, if the first cooling down of the fuel had not gone so far that the wax had crystallised out to an appreciable extent, the asphaltenes still separated out in such a way that, on heating up the fuel again afterwards, and cooling it again, a rise in flow-point caused by the removal of asphaltenes might occur. The answer to this question might be of importance in order to know what may be expected under corresponding changes of temperature in practice.

Mr. W. A. Woodrow said he believed it was the intention of the Authors to try to evolve a test which approximated more or less closely to changes in temperature which the fuel might undergo in works practice, but in their suggested test he noticed that the oil was warmed first, then cooled down to 0° C., and then raised by about 1° C. per three to four minutes. To his mind that seemed to be the reverse of ordinary works practice, where the fuel oil would be subjected to a cooling change rather

than to an increasing temperature. It therefore did not seem that the Authors had achieved the task of evolving a test approximating to conditions of works practice.

Mr. E. A. Evans said he noticed that the Authors explained very fairly that the thermal history had a tremendous influence on the ordinary pour-point test, and apparently, according to their findings, it was equally applicable to the I.P.T. setting-point. Would it not equally apply to the new method which the Authors had suggested? He would like to say that any papers published which would finally result in the execution of the test would, he was sure, be very much appreciated by all those concerned with the subject.

Mr. J. S. Jackson said that the Authors' test, in common with many other tests, seemed to aim at measuring the lowest temperature at which the oil would flow. He believed that it was more important to determine the temperature at which the oil could be filtered. Diesel-engine fuel, for instance, had to be filtered in order to get rid of minute quantities of extraneous matters. If the filters were choked with relatively small quantities of paraffin wax crystals, there was a danger that the engineer would remove the filter, and thereby give rise to a variety of troubles. In the absence of a standard test, he had been carrying out a simple filtering test at 32° F.

The Authors, in reply, wrote as follows:—

As to the first comment of Mr. McConnell Sanders, it is thought that, in mixed-base crude fuels, the two phenomena by which the pour-point is reached—increase in viscosity of the oil which possibly contains dissolved paraffin wax, and crystallising out of the wax—may co-operate, especially if the viscosity is rather high.

They fully agree with the comments on the difficulties of standardization.

Only few concrete data are at the Authors' disposal on a fuel oil's memory for treatment at high temperatures. In so far as they know, this is very great; in some cases they have seen samples which experienced a favourable influence even after 1½ years. (See also the experiment on p. 163.) On the other hand, a heating of the cooled fuel from 10° or 20° C. to about 35° C., followed by cooling, is sufficient to make the oil forget its preheating to 100° C.

The Authors do not preclude the possibility of distillates containing asphaltenes, or, generally speaking, natural pour-point reducers. They do not, however, think that these quantities will be great enough to reduce the pour-point to any appreciable extent. The phenomenon described by Mr. McConnell Sanders has also been observed by them in a somewhat analogous case. In this instance there was, however, every reason to assume that the cause was attributable to the lower solubility of the paraffin wax in the oil, from which the aromatics had been removed. The Authors do not know whether this explanation also applies to the case described by Mr. McConnell Sanders; in particular, they cannot say to what extent the extraction of the aromatics from the distillate in the case referred to by him was great enough to make the above explanation plausible.

In reply to Mr. Brocades Zaalberg, for the determination of the flow-point the oil is pretreated, as explained in the paper, to eliminate the influence of the asphaltenes on the flow-point. This pretreatment consists in cooling to 0° C., followed by heating to 35° C. 0° C. is admittedly lower than strictly necessary for a complete elimination of this influence, but this temperature has been chosen because it is a convenient one from a laboratory point of view, and gives an ample safety margin so as to ensure actual attainment of the purpose in view.

From the data given below, it follows that there are also fuels for which cooling to about 20° C., followed by heating to 35° C., is already sufficient to eliminate this influence :—

Heated to 100° C.,	cooled to	30° C.,	heated to	35° C.,	fl.-pt.	<	− 30° C.
„	„	„	25° C.,	„	„	„	− 20° C.
„	„	„	22½° C.,	„	„	„	− 9° C.
„	„	„	20° C.,	„	„	„	− 5° C.
„	„	„	0° C.,	„	„	„	− 5° C.

Of the same oil the pour-point was determined.

Heated to 100° C.,	cooled to	30° C.,	heated to	35° C.,	p.-pt.		− 23° C.
„	„	„	25° C.,	„	„	„	+ 7° C.
„	„	„	20° C.,	„	„	„	+ 21° C.
„	„	„	0° C.,	„	„	„	+ 20° C.

The Authors consider it probable that, to render the asphaltenes completely inactive, it is actually essential that the bulk of the paraffin wax should have separated out from the solution, thus extracting at the same time the larger portion of the asphaltenes from the oil.

In practice, the case can therefore very readily occur that the thermal history of a sample is such that the pour-point reducing effect of the asphaltenes has been lost. For this to occur it is sufficient for some fuels to be heated from 20° C. to 35° C. before being exposed to a temperature below their pour-point.

In reply to Mr. W. A. Woodrow's remarks, the Authors tried to imitate the worst temperature conditions possible under actual working conditions, and they think that heating the oil from perhaps 10° C. to about 30–40° C., then cooling to 0° C., is what will often happen to an oil in actual practice—for instance, when a plant using fuel oil which heats the oil to about the critical temperature range (viz. 30–40° C.), to get the right viscosity, shuts down on Saturday and starts again on Monday, thus giving exactly the temperature treatment which is most unfavourable to the behaviour at low temperature.

The Authors quite agree with Mr. Evans that their method of determining the flow-point cannot get away from the temperature sensitivity of the fuel. For this reason they have chosen a pretreatment which gives them the *true maximum* flow-point of the curve flow-point—temperature of pretreatment (experiments 1, 2, and 3).

In reference to Mr. Jackson's remarks about filtering, it was admitted that filtering difficulties with Diesel oil were caused by small traces of paraffin wax crystals, and a pour-point test, or any other test proposed to replace it, could not possibly give an indication of the difficulties that might be encountered. Their experience of filtration tests was not so good as Mr. Jackson's experience seemed to be; they had very unpleasant

recollections of doing filtration tests. Of course, they must give an indication; if the oil clogged the filter in the laboratory it was sure to clog a Diesel oil filter.

On the motion of **The President**, a hearty vote of thanks was accorded to Mr. Moerbeek and Mr. van Beest for their valuable paper, and the meeting then terminated.

RELATIVE EFFICIENCIES OF PACKED FRACTIONATING COLUMNS.

By P. Docksey, B.A. (Associate Member), and
C. J. May, Ph.D., A.R.C.Sc., A.I.C.*

Summary.

On the assumption that the rate of interchange of material between vapour and liquid in a fractionating column depends on the rate of diffusion through that part of the vapour in which the flow is streamline, it is possible to derive equations from which the relative efficiencies of columns packed with material of any given shape may be calculated. These equations apply both to the case in which the flow of the vapour is streamline, and to that in which it is turbulent, and allow the effect of alteration of pressure and vapour velocity and the introduction of diluent such as steam to be calculated.

Experiments on packed columns are described which were designed to check both the streamline flow and turbulent flow formulæ. The experimental results give good agreement with the theory and indicate that the initial assumption is valid.

Introduction.

The efficiencies of packed fractionating columns have formed the subject of several papers in the literature. The method by which the determinations have been made is the same in all cases—namely, to fractionate in the column a binary mixture for which the vapour–liquid equilibrium curve is known, and from analysis of the material in the still and the product to deduce the number of theoretical plates in the column.

The binary mixtures which have been used are :

Water–methyl alcohol.
„ –ethyl alcohol.
„ –nitric acid.
„ –acetic acid.
Benzene–toluene.
„ –carbon tetrachloride.
Chloroform–toluene.

Various types of packing have been investigated, including glass beads and cylinders, glass chips, jack chain and Lessing rings.

The determinations have all been carried out at atmospheric pressure, and there is agreement that the efficiency of packing materials of similar shape varies inversely as the diameter of the packing. The effect of variables such as pressure and the introduction of diluent such as steam or nitrogen have not been investigated. There is disagreement as to the effect of vapour velocity. Peters [1] gives no figures for the vapour velocity in his experiments. Leslie and Geniesse [2] report that it is without effect. Hill and Ferris [3] examined several types of packing, and found that increasing the

* Communication from the Anglo-Persian Oil Company's Research Laboratory, Sunbury. Paper received September 9th, 1934.

vapour velocity increased the efficiency. A distillation apparatus for small samples was constructed by Cooper and Fasce,[4] and they found that the fractionation is improved by decreasing the vapour velocity, while Kostrin [5] obtained similar results, and states that the efficiency varies inversely as the velocity.

In view of the fact that packed columns are frequently used under vacuum and with steam, it is important to make some estimation of the effect which these alterations in the physical conditions will have on the number of plates. In the following paper, formulæ are derived from which the variations in the number of theoretical plates due for changes in pressure and velocity in the column may be estimated. No attempt is made to apply the results to bubble plate columns, since although the means by which material is transferred from the liquid to the vapour and vice versa is probably the same, other factors, such as the time of contact between vapour and liquid and the degree of turbulence inside a bubble, are ambiguous.

Experiments designed to check the formulæ are also described.

The basic idea of the calculation is that the rate of interchange of material from the one phase to the other is entirely governed by diffusion in that portion of the vapour in which the flow is streamline. This may be throughout the entire cross section of the column in a case in which the diameter is small and the vapour velocity low, or through a streamline layer at the interface when flow is turbulent.

It may be that this is not the factor which controls the interchange: diffusion through the liquid reflux layer, or the disturbance of the stagnant layer of vapour next to the liquid film owing to ebullition, may mask the effects of diffusion in the vapour.

However, the agreement between the formulæ and the experimental results show that the diffusion in the vapour phase is the main factor. Furthermore Hollings and Silver, in a paper [6] published while this work was in progress, show that similar considerations are applicable in the case of washing a gas.

Part I.—Derivation of Equations.

The following assumptions are made:—

(1) A mixture of two liquids designated A and B is distilled in the column. The two liquids have different boiling points, but the density, mean free path, etc., are the same. This assumption could be discarded, but only at the expense of making the calculation much more complicated.

(2) The term "concentration" is defined as the weight of one of the components in grams contained in one millilitre of the vapour.

(3) The term "composition" is defined as the weight of one of the components in grams in one gram of the vapour. Therefore concentration = composition $\times \rho$, where ρ is the density of the vapour.

(4) Distribution of composition in streamline flow. In two columns which are of different dimensions, but geometrically similar, in which the flow is streamline, it is possible to select corresponding sections at which the mean vapour composition is the same, and at which the variations of

composition across the section are geometrically similar. It is shown that if this is so at any point, the variation in composition will be similar at all corresponding points throughout the column.

(5) Distribution of composition in turbulent flow.

In this case it is assumed that there is a thin streamline layer next to the liquid reflux, and that the central core is of uniform composition, *i.e.* is perfectly mixed. This assumption is dealt with more fully later.

(6) The vapour at the surface of the reflux is in equilibrium with it. In conjunction with (4) this indicates that the compositions of the vapour at the vapour reflux surface are the same at corresponding sections.

(7) The reflux on the wall at any section is of uniform composition, *i.e.* diffusion of material through the reflux is rapid, or the action of flowing over the walls stirs the reflux.

(8) The vapour–liquid equilibrium curve is the same for the mixtures used in the two columns, and is not affected by pressure. (This assumption again could be dispensed with at the expense of a more involved calculation.) As far as a comparison of the fractionating efficiencies at different pressures is concerned, this assumption has the effect of neglecting the increased ease of separation introduced by vacuum distillation when distilling hydrocarbons.

(9) The disturbances to flow at the entrance to and exit from the columns are neglected.

(10) The Height Equivalent to a Theoretical Plate (H.E.T.P.) [1] is proportional to the height necessary to produce the same small change in composition in the two columns.

Nomenclature.—The following symbols are used throughout the paper:

C	Concentration, grms. of particular component/ml. of vapour.
x & y & z	Composition, grms. of particular component/grm. of vapour.
ρ	Density of vapour, grms./ml.
η	Absolute viscosity, grms./cm./sec.
λ	Molecular mean free path, cm.
S	Effective molecular diameter, cm.
S_{12}	Mean molecular diameter of two substances, cm.
N	Number of molecules/ml.
M	Molecular weight, grms.
T	Temperature, ° K.
V	Molecular root mean square velocity, cm./sec.
u	Vapour velocity, cm./sec.
$u_m = v$	Mean vapour velocity, cm./sec.
R	Gas constant.
p	Pressure, dynes/sq. cm.
Δ	Diffusion coefficient, cm.²/sec.
h	Column height, cm.
r	Column radius, cm.
D	Column diameter, cm.

Diffusion Coefficient and Viscosity of Mixtures.—Certain physical properties of the vapour are required in the calculation. The formulæ used are taken from the standard dynamical theory of gases, but in some cases are subject to a certain amount of doubt—as, for example, in the case of the viscosity of a mixture of vapours. Since, however, we are concerned only with comparative results, the use of consistent formulæ throughout will in general not affect the ultimate conclusions.

(1) *Viscosity.*—For the viscosity of a pure vapour (or a mixture of two vapours of very similar physical properties) the formula

$$\eta = \frac{0{\cdot}499\rho V}{\sqrt{2}\pi N S_{11}^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

is taken.

For a mixture in which the components differ greatly in physical properties (as, for example, occurs in a normal steam distillation) Kuenen's formula [7] has been simplified to

$$\eta = \Sigma \frac{\eta_1}{\left[1+0{\cdot}222\left(1-\frac{M_1}{M_1+M_2}\theta_{12}\right)\right]\frac{x_2}{x_1}\left[1+\left(\frac{\eta_1}{\eta_2}\right)^{\frac{1}{2}}\left(\frac{M_2}{M_1}\right)^{\frac{1}{4}}\right]^2\left(1+\frac{M_1}{M_2}\right)^{\frac{1}{2}}} \quad . \quad (2)$$

where η is the viscosity of a pure component and θ_{12} is taken from Jean's theory of the persistence of velocities.

(2) *Diffusion Coefficient.*—In dealing with steam distillation it is necessary to consider diffusion in a mixture of three components, one of which (the inert diluent) is of uniform concentration throughout the whole mass of vapour. There appear to be no experimental results published, and Meyer's formula (corrected for persistence of velocities) has therefore been modified to suit the case. The two diffusing components are assumed to have the same molecular weight and size, and we then have

$$\Delta = \frac{V}{3\pi\left[0{\cdot}594\sqrt{2}(N_1+N_2)^2 S_{11}^2 + (1-\theta_{13})N_3 S_{13}^2\left(1+\frac{M_1}{M_3}\right)^{\frac{1}{2}}\right]} \quad . \quad (3)$$

In the absence of the third component this reduces to

$$\Delta = \frac{0{\cdot}395V}{\pi S_{11}^2(N_1+N_2)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

This formulæ is not strictly correct, since it yields a ratio

$$\frac{\Delta\rho}{\eta} = 1{\cdot}12$$

instead of 1·34. The ratio is, however, constant, and for comparative purposes its exact value is immaterial.

Derivation of Equation for Streamline Flow and Turbulent Flow at Constant Reynolds Number.—The calculation is made for a column consisting of a plain cylindrical tube. The variation of concentration in the vapour is examined, both with height up the column and across the cross section, and it is shown that if in two columns the concentration distributions are the same at any height, they will remain so throughout the column. An equation is then derived which is applicable to columns in streamline flow, and which may also be used in the case of turbulent flow when comparing two columns which are working at the same Reynolds number.

Consider a column consisting of an empty cylindrical tube of radius r and height h, and suppose a binary mixture to be distilled, the two components being of the same molecular weight M and component A boiling at a higher temperature than component B.

Now, at any horizontal cross section of the column the concentration of the component A will vary across the section; let this concentration be C_a at a distance a from the centre.

If it be assumed that there is no discontinuity at the wall of the tube where a thin film of reflux is flowing downwards at a uniform rate, and that the vapour immediately in contact with the liquid is everywhere in equilibrium therewith, then the rate at which the component A is absorbed by the liquid will be proportional to the concentration gradient at the surface; and in a small element of height dh will be

$$2\pi r dh\Delta \frac{dc_r}{dr} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where Δ is the diffusion coefficient.

Now consider an annulus distance a from the centre; it is required to determine the change in concentration at this annulus with the height of the column, *i.e.* $\frac{dc_a}{dh}$. If flow in the column is streamline, the annulus may be taken anywhere; if turbulent, the calculation will apply only within the small streamline region close to the wall of the tube.

If u is the actual linear velocity at the annulus

$$u = \frac{1}{4\eta}\frac{dp}{dh}(r^2 - a^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where η is the viscosity of the vapour and $\frac{dp}{dh}$ the pressure drop/unit length.

The net loss of component A from the annulus in unit time is the difference between the amount diffusing across the inner and outer surfaces.

i.e.
$$2\pi(a + da)dh\Delta \frac{dc_{(a+da)}}{da} - 2\pi a dh\Delta \frac{dc_a}{da}$$
$$= 2\pi\Delta\left(\frac{dc_a}{da} + a\frac{d^2c_a}{da^2}\right)dadh$$

The total volume of vapour passing upwards through the annulus in unit time is

$$2\pi a(da)u = \frac{\pi a(da)}{2\eta}\frac{dp}{dh}(r^2 - a^2)$$

$\therefore$ the rate of change of concentration with height

$$\frac{dc_a}{dh} = \frac{4\eta\Delta}{a\frac{dp}{dh}(r^2 - a^2)}\left(\frac{dc_a}{da} + a\frac{d^2c_a}{da^2}\right) \quad . \quad . \quad . \quad . \quad (7)$$

or
$$dh = \frac{a\frac{dp}{dh}(r^2 - a^2)dc_a}{4\eta\Delta\left(\frac{dc_a}{da} + a\frac{d^2c_a}{da^2}\right)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Now consider two columns of different dimensions working at the same pressure and with the same binary mixture. Assume that at some cor-

responding section of the two columns at which the mean vapour compositions are equal, the concentration distributions across the horizontal section are geometrically similar,

i.e. $c_{a_1} = c_{a_2}$ when $\frac{a_1}{a_2} = \frac{r_1}{r_2}$ *i.e.* $a_2 = \frac{r_2}{r_1} a_1$ and $da_2 = \frac{r_2}{r_1} da_1$

Whence at these corresponding radii

$$\frac{a_1}{a_2}\left(\frac{dc_a}{da}\right)_1 = \left(\frac{dc_a}{da}\right)_2 \text{ and } \left(\frac{a_1}{a_2}\right)^2\left(\frac{d^2c_a}{da^2}\right)_1 = \left(\frac{d^2c_a}{da^2}\right)_2$$

from equation (8) therefore the ratio of the heights for a given change in concentration at the annulus is

$$\frac{dh_1}{dh_2} = \frac{a_1\left(\frac{dp}{dh}\right)_1\left(r_1^2 - a_1^2\right)\left[\left(\frac{dc_a}{da}\right)_2 + a_2\left(\frac{d^2c_a}{da^2}\right)_2\right]}{a_2\left(\frac{dp}{dh}\right)_2\left(r_2^2 - a_2^2\right)\left[\left(\frac{dc_a}{da}\right)_1 + a_1\left(\frac{d^2c_a}{da^2}\right)_1\right]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$= \frac{a_1^4\left(\frac{dp}{dh}\right)_1}{a_2^4\left(\frac{dp}{dh}\right)_2} = \frac{r_1^4\left(\frac{dp}{dh}\right)_1}{r_2^4\left(\frac{dp}{dh}\right)_2} \quad = \text{constant irrespective of the value of } a \quad . \quad . \quad . \quad . \quad . \quad (10)$$

It follows that if at any section of the two columns the distributions of concentrations over the streamline region are geometrically similar, they will remain so on passing up the column, a height proportional to $r^4\left(\frac{dp}{dh}\right)$ being necessary to effect a given change in concentration, *i.e.* for a given degree of fractionation. Now consider two columns of equal diameters, but working at different pressures. The concentrations at equal radii of corresponding cross sections are evidently proportional to the pressures, as are also the values of $\frac{dc_a}{da}$ and $\frac{d^2c_a}{da^2}$.

Equation (9) therefore becomes

$$\frac{dh_1}{dh_2} = \frac{a_1\left(\frac{dp}{dh}\right)_1\left(r_1^2 - a_1^2\right)\left[\left(\frac{dc_a}{da}\right)_1 + a_1\left(\frac{d^2c_a}{da^2}\right)_1\right]\eta_2\Delta_2 p_2 (dc_a)_1}{a_2\left(\frac{dp}{dh}\right)_2\left(r_2^2 - a_2^2\right)\left[\left(\frac{dc_a}{da}\right)_2 + a_2\left(\frac{d^2c_a}{da^2}\right)_2\right]\eta_1\Delta_1 p_1 (dc_a)_2} \quad . \quad (11)$$

where p_1 and p_2 are the operating pressures.

This expression is again independent of the value of a, so that geometrical similarity holds throughout the column. In order, however, to obtain the same degree of fractionation in each case, $p_2(dc_a)_1$ must equal $p_1(dc_a)_2$, since under these conditions the changes in composition will be equal. Hence

$$\frac{dh_1}{dh_2} = \frac{\eta_2\Delta_2\left(\frac{dp}{dh}\right)_1}{\eta_1\Delta_1\left(\frac{dp}{dh}\right)_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Combining equations (9) and (11), and remembering that

$$\frac{dp}{dh} = \frac{\rho u_m^2}{D} f\left(\frac{u_m D \rho}{\eta}\right)$$

where $D = 2r$ and u_m is the mean velocity, for a given degree of fractionation

$$h \propto \frac{\rho u_m^2 D^2}{\eta \Delta} f\left(\frac{u_m D \rho}{\eta}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Application to Streamline Flow.—If geometrical similarity can be assumed irrespective of the value of the Reynolds number, then

$$f\left(\frac{u_m D \rho}{\eta}\right) \propto \frac{\eta}{u_m D \rho}$$

and

$$h \propto \frac{u_m D^2}{\Delta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

from equation (13) assuming equal sizes and masses for the molecules

$$\Delta = \frac{0{\cdot}395 V}{\pi N S_{11}^2}$$

and

$$h \propto \frac{u_m D^2 N S_{11}^2}{V}$$

Hence for the same pair of liquids being distilled

(i) Altering D, u_m constant—$h \propto D^2$
(ii) Altering u_m, D constant—$h \propto u_m$
(iii) Altering pressure but maintaining the same weight throughput

$$W = \frac{\pi D^2 \rho u_m}{4}$$

$$h \propto \frac{N}{V\rho}$$

or since

$$N \propto \rho$$

$$h \propto \frac{1}{V}$$

and independent of the pressure except in so far as the temperature is affected, h being proportional to $T^{-\frac{1}{2}}$.

(iv) If a diluent gas is introduced, W being kept constant, u_m is also constant

$$h \propto \frac{1}{\Delta}$$

the value of Δ being given by equation (3).

Application to Turbulent Flow at Constant Reynolds Number.—It cannot be assumed that similarity will hold save at the same Reynolds number (the composition of the vapour in the turbulent core is assumed uniform

over the section, and therefore the geometrical similarity holds in this region). If $\frac{u_m D\rho}{\eta}$ is constant

$$h \propto \frac{\rho u_m^2 D^3}{\eta\Delta} \propto \frac{u_m D^2}{\Delta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

This is identical with equation (21) derived below for any condition of turbulent flow if $\frac{vD\rho}{\eta}$ is made constant.

Derivation of General Equation for Turbulent Flow.—The case of turbulent flow is not easy to deal with exactly, but it is possible to derive an equation by taking into account the fact that the mechanism of heat flow from the wall of a tube is an interchange of molecules between the surface layers and the bulk of the gas, and is therefore similar to the transfer of material from the surface to the mass.

For a gas flowing under turbulent conditions in a tube the following equation has been found to hold

$$\frac{HD}{K} = \beta\left(\frac{vD\rho}{\eta}\right)^{0.8}$$

where H = conductance, cal./sq.cm./sec.
K = conductivity, cal./sq.cm./cm./sec.
D = tube diameter.
β = constant.

Now, if we make the assumption that there is a central core of gas which is perfectly mixed, and a thin layer on the wall in streamline flow through which heat passes by conductivity, the thickness of this layer (assumed small compared with D) is equal to

$$\frac{K}{H} = \frac{D}{\beta\left(\frac{vd\rho}{\eta}\right)^{0.8}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Now, in the case of a fractionating column, if at any point the concentration of component A in the central core is c and at the wall is c_r, the mean concentration gradient is

$$\frac{(c - c_r)\beta\left(\frac{vd\rho}{\eta}\right)^{0.8}}{D} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

To obtain $\frac{dc}{dh}$ we have

Mass diffusing across streamline layer in height dh in unit time

$$= 2\pi r dh \frac{(c - c_r)\beta\left(\frac{vd\rho}{\eta}\right)^{0.8}\Delta}{D} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

where Δ is the diffusion coefficient.

Total volume of vapour passing vertically in unit time in core

$$= \pi r^2 v$$

$$\therefore \frac{dc}{dh} = \frac{2\pi r(c - c_r)\beta\left(\frac{vd\rho}{\eta}\right)^{0\cdot8}\Delta}{\pi r^2 vD} \quad . \quad . \quad . \quad . \quad . \quad (19)$$

or

$$dh = \frac{vD^2}{8(c - c_r)\beta\left(\frac{vD\rho}{\eta}\right)^{0\cdot8}\Delta}\, dc \quad . \quad . \quad . \quad . \quad . \quad (20)$$

If therefore at corresponding sections of two columns working at the same pressure the concentrations c and c_r are the same, the similarity will persist in passing up the column, the equivalent heights being proportional to

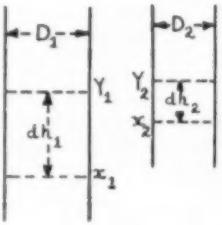
$$\frac{vD^2}{\Delta\left(\frac{vD\rho}{\eta}\right)^{0\cdot8}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

If one column is working at a reduced pressure or (in the presence of a diluent) at a reduced partial pressure, and we take corresponding sections at which c is proportional to the pressure, we require a change in concentration dc also proportional to the pressure for the same degree of fractionation, so that, as in the case of streamline flow, the equivalent height is not altered by the pressure.

For example, consider the two columns depicted below, the same binary mixture being distilled in each, but at different pressures, x and y being corresponding sections.

Column 1.

Pressure $= p_1$.
Properties of vapour ρ_1, η_1, Δ_1.
Composition of vapour in core x grms. of component A/grm. at x_1.
Y grms. of component A/grm. at Y_1.
Mean composition of vapour at surface of reflux over height $dh_1 = z$ grms. A/grm.



Column 2.

Pressure $= p_2$.
Properties of vapour ρ_2, η_2, Δ_2.
Composition of vapour in core x grms. A/grm. at x_2.
Y grms. A/grm. at Y_2.
Mean composition of vapour at surface of reflux over height $dh_2 = z$ grms. A/grm.

The concentrations of A in grms./ml. are evidently $x\rho_1$, $x\rho_2$, etc. The weights of the vapours in the two cases flowing per unit time are $\frac{\pi D_1^2}{4} v_1\rho_1$ and $\frac{\pi D_2^2}{4} v_2\rho_2$.

The weights of component A transferred to the well are therefore

$$\frac{\pi D_1^2}{4} v_1\rho_1(y - x) \text{ and } \frac{\pi D_2^2}{4} v_2\rho_2(y - x).$$

The mean concentration gradients are proportional to

$$\rho_1 \frac{(x+y-2z)}{2} \frac{\left(\frac{v_1 D_1 \rho_1}{\eta_1}\right)^{0\cdot 8}}{D_1} \text{ and } \rho_2 \frac{(x+y-2z)}{2} \frac{\left(\frac{v_2 D_2 \rho_2}{\eta_2}\right)^{0\cdot 8}}{D_2}$$

since the thickness of the streamline layer is proportional to

$$\frac{D}{\left(\frac{vD\rho}{\eta}\right)^{0\cdot 8}}$$

The weights diffused are proportional

$$\pi D_1 dh_1 \frac{dc_1}{da} \Delta_1 \text{ and } \pi D_2 dh_2 \frac{dc_2}{da} \Delta_2$$

$$i.e. \quad dh_1 \propto \frac{\frac{\pi D_1^2}{4} v_1 \rho_1 (y-x)}{\pi \Delta_1 \rho_1 \left(\frac{x+y-2z}{2}\right)\left(\frac{v_1 D_1 \rho_1}{\eta_1}\right)^{0\cdot 8}} \propto \frac{v_1 D_1^2 (y-x)}{\Delta_1 (x+y-2z)\left(\frac{v_1 D_1 \rho_1}{\eta_1}\right)^{0\cdot 8}}$$

with a similar expression for dh_2.

Whence, eliminating the constants

$$h \propto \frac{vD^2}{\Delta \left(\frac{vD\rho}{\eta}\right)^{0\cdot 8}}$$

we have then the following effects on efficiency by altering the various factors.

(1) Altering diameter, v and p constant

$$h \propto D^{1\cdot 2}$$

(2) Altering velocity, D and p constant

$$h \propto v^{0\cdot 2}$$

(3) Altering pressure, D constant

$$h \propto \frac{v^{0\cdot 2} \eta^{0\cdot 8}}{\Delta \rho^{0\cdot 8}}$$

or, since $\Delta \propto \frac{\eta}{\rho}$

$$h \propto \left(\frac{v\rho}{\eta}\right)^{0\cdot 2}$$

That is for the same weight throughput $v\rho$ = constant and the height varies only slightly due to the change in η with temperature.

(4) $\frac{vD\rho}{\eta}$ constant

$$h \propto \frac{vD^2}{\Delta}$$

(5) Introducing diluent, D constant and same weight of vapour/sec. at the same partial pressure, v is constant

$$h \propto \frac{1}{\Delta}\left(\frac{\eta}{\rho}\right)^{0.8}$$

The value of Δ must be obtained from equation (3). In general, the decrease in Δ will outbalance the corresponding increase in ρ, and leads to a relatively considerable increase in h (*i.e.* reduction in column efficiency).

With regard to the question of the effect of a diluent, two points should be particularly noted. In the first place, formula (3) for the diffusion coefficient has not been experimentally tested, and might be subject to some later modification. But, in any case, if the mechanism of transfer assumed in this paper is correct, there can be no doubt that the introduction of a diluent will tend to reduce efficiency, and at least the order of the change in diffusion coefficient will be given by equation (3). Secondly, there are very little data on the viscosity of gaseous mixtures. Such as there are indicate that any type of variation is possible—a mean between the viscosities of the two components, a viscosity mainly controlled by that of one component, and a viscosity slightly greater than that of either component. This factor does not enter into the formula for streamline flow, but has a marked effect in the case of turbulent flow.

Effect of Heat Transfer.—It is evident that in order to obtain fractionation, heat as well as material must be transferred from the vapour to the reflux, a given degree of fractionation requiring a definite amount of heat to be transferred. Starting from the accepted equations for heat transfer, in the absence of a diluent, formulæ can be derived for the relative efficiencies of columns similar to those obtained above by a consideration of material transfer.

For turbulent flow we get

$$dh \propto \frac{vD^2}{\frac{K}{\rho}\left(\frac{vD\rho}{\eta}\right)^{0.8}} \frac{dt}{T-t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

where K is the conductivity of the vapour.
dt the change in temperature of the reflux for a given degree of fractionation
T and t are the temperatures of vapour and reflux respectively.

Now, in the absence of a diluent, $\frac{K}{\rho}$ is proportional to Δ, and comparison with equation (21) indicates that $\frac{dt}{T-t}$ must be constant and possess a specific value if the transfer of both heat and material are to be in equilibrium. Normally this assumption is compatible with the heat balance in the column and the assumed properties of the mixture being distilled.

If, however, a diluent is introduced, $\frac{K}{\rho}$ is no longer proportional to Δ, and since the heat capacity of the vapour is increased, $\frac{dt}{T-t}$ cannot be

constant. In other words, equations (21) and (22) cannot be simultaneously true under the postulated conditions, which require a constant reflux ratio throughout the column. Some evaporation of the reflux must occur—mostly at the bottom of the column—this constituting an "end effect" with which the present paper does not profess to deal. The magnitude of the effect is, however, small. The maximum amount of evaporation which can take place is calculable from a knowledge of the extra heat input to the column carried by the diluent and of the latent heat of the reflux. In normal practice this will not exceed 5 per cent. of the reflux; a similar effect would be obtained by slightly superheating the vapour from the still.

Precisely analogous considerations apply to the case of streamline flow.

Part II.—EXPERIMENTAL.

The following experiments were carried out in order to test the formulæ developed in the first part of the paper. They may be divided into two parts:—

(1) *Tests on Column of 8 mm. Internal Diameter.*

This column consisted of a glass tube 8 mm. I.D. 100 cms. long fitted with a spiral packing made from copper strip. The flow of the vapours was streamline at the lower rates used, and the experiments show the influence of linear velocity on the column efficiency in the streamline region.

Description of Apparatus.—The still consisted of a bolt-head flask of 400 ml. capacity which was heated on an open bowl type of electric heater. The top of the flask was lagged with thick asbestos sheet. The column was inserted through a cork in the neck of the flask, and a thermometer was placed in the vapour space.

The column was lagged electrically, and the heater was divided into two independently controlled sections. Two thermocouples brazed on to the surface of short copper cylinders placed inside the electric winding allowed the heat loss from the column to be accurately compensated. The lagging was arranged so that the interior of the column could be observed.

A small glass flow-meter of the orifice type was placed in the top of the column, and served to measure the reflux rate. The electrical lagging was carried up above the meter, so that errors in the estimation of the reflux ratio due to condensation below the meter were avoided.

The column head was inserted through a cork in the top of the column. The distillate was totally condensed in a glass double-surface condenser, and ran back into the column head, where it was caught in a gallery. From this gallery any desired quantity of liquid could be withdrawn through a side arm fitted with a glass stop-cock; the remainder spilled over the side of the gallery into the reflux meter. It was assumed that this reflux was at its boiling-point. A thermometer was placed in the column head to measure the top temperature. The thermometers in the column head and in the vapour space of the flask were carefully calibrated, and the necessary stem corrections applied.

The liquid distillate run off from the column head through the side arm passed through a cooler to a measuring cylinder.

Experimental Method.—The H.E.T.P. was estimated using a benzene-toluene mixture, the composition at the top and bottom of the column being estimated from the temperature, and the number of plates being determined by McCabe and Thiele's method.[8]

The experimental procedure was as follows: 200 ml. of benzene–toluene mixture of appropriate composition were charged into the still. The two components were carefully purified and dried before mixing. The electric heating was switched on and the heat loss winding adjusted. The draw-off tap at the column head was closed and the column operated under total reflux, the heating of the still being regulated so as to give the desired vapour velocity in the column, and readings were then taken of the top and bottom temperatures, and the number of plates was estimated. The heating was then altered so as to allow observations to be made at another vapour velocity in the column.

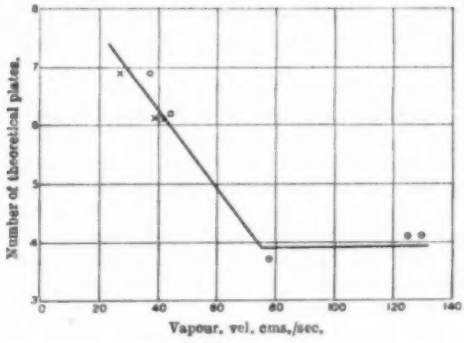


FIG. 1.

RELATION BETWEEN VAPOUR VELOCITY AND NUMBER OF PLATES.

If it was desired to work at any other reflux ratio than total, the appropriate quantity of distillate was run off from the column head.

Results.—Fig. 1 shows the number of plates in this column plotted against the linear velocity of the vapour. The latter was calculated assuming the column to be a plain tube, *i.e.* neglecting the volume of the packing.

In order to make some estimate of the type of flow occurring in the 8 mm. column under the conditions used, water was passed up a 14 mm. I.D. column of geometrically similar construction, at such speeds as to make $\frac{vD\rho}{\eta}$ the same in the two cases. The flow was observed by introducing a thin stream of coloured liquid in the well-known manner. It was found that the flow at the lower rates was streamline, with a small amount of eddying over the edges of the packing, gradually increasing to turbulence at the higher rates.

It will be seen from Fig. 1 that the H.E.T.P. varies roughly as v at the lower rates of flow, which is in agreement with the formula for streamline flow.

(2) *Tests on 2-in. I.D. Column Packed with Lessing Rings.*

These experiments were designed to test the turbulent flow formula and covered variations in pressure and velocity, and the introduction of diluent.

Binary Mixture Used.—The binary mixtures normally used for experiments such as these are not suitable for working under low pressure, on account of the low temperatures necessary to effect condensation, and

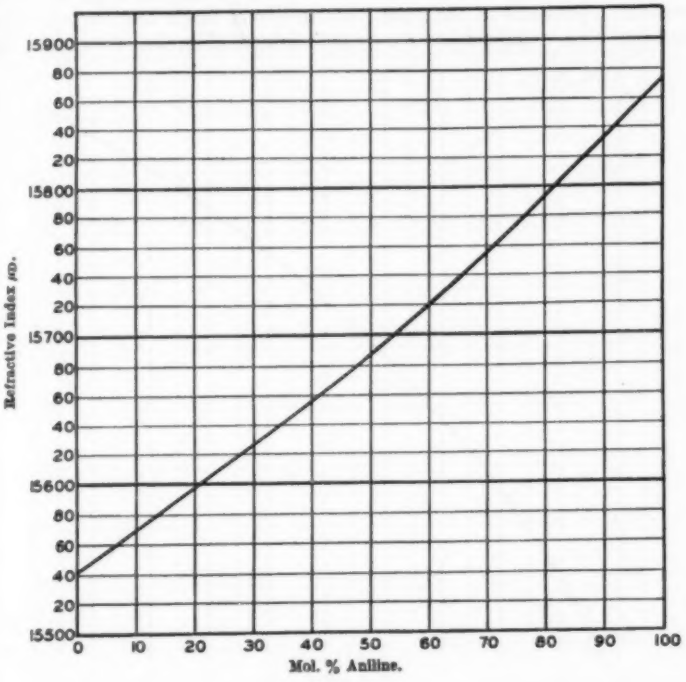


FIG. 2.

REFRACTIVE INDICES OF NITROBENZENE–ANILINE MIXTURES.

after some consideration it was decided to use a mixture of nitrobenzene and aniline. The desirable characteristics of suitable mixtures are :—

(1) The compounds used must be miscible in all proportions, and must not react chemically with each other.

(2) They should not form a constant-boiling mixture.

(3) The mixtures must be capable of being accurately analysed.

(4) The molal latent-heats should be as close as possible.

When pure nitrobenzene and aniline are mixed, the solution has a red colour. This is apparently due to the formation of a small quantity of a highly-coloured compound which has not been isolated, and about which very little is known. The vapour–liquid equilibrium curve for the mixtures

is normal, and the boiling-point and refractive index curves show no unusual features. It was concluded that the effect on the experimental results of the formation of this small quantity of a loose molecular compound would be negligible. In other respects the nitrobenzene–aniline mixtures fulfil the requirements excellently.

Nitrobenzene and aniline (A.R. grade) were therefore re-distilled using a column consisting of 36 in. of $\frac{1}{4}$-in. Lessing rings. The refractive indices of the middle fractions corresponded exactly with those given in the literature. Mixtures of the pure materials were made and the refractive index-per cent. composition curve determined (Fig. 2), using an Abbé

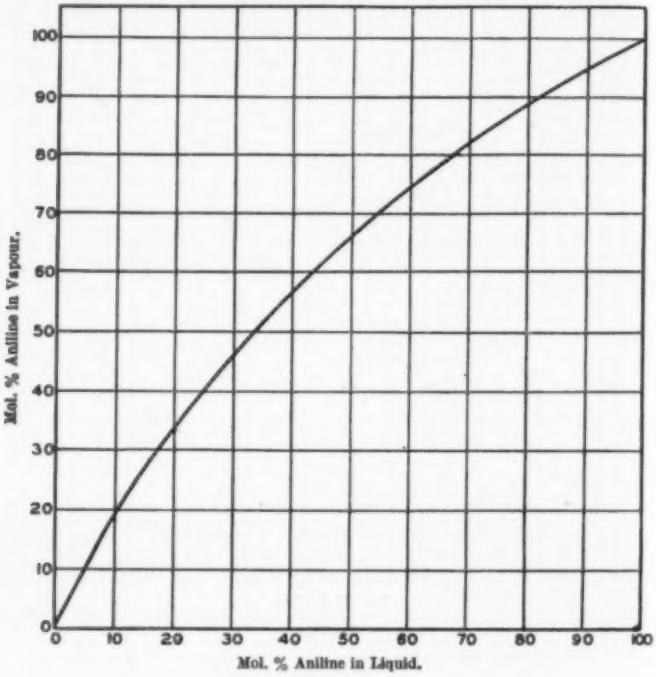


FIG. 3.

NITROBENZENE–ANILINE EQUILIBRIUM CURVE AT 10 MM. PRESS.

refractometer. By means of this curve the mixtures could be analysed with an accuracy of $\frac{1}{2}$ per cent. It was found that during the experiments the mixture in the still tended to darken badly; separate experiments showed that if a discoloured mixture was distilled as nearly to dryness as possible, an accurate analysis of the mixture was obtained by determining the refractive index of the distillate.

Further mixtures were made up, and the vapour liquid equilibrium curve at 10 mm. pressure was determined using the method of Rosanoff, Bacon and White [9] (Fig. 3). A further determination of the equilibrium

curve was made at 253 mm. pressure (Fig. 4). This pressure was chosen because in some experiments carried out at atmospheric pressure nitrogen was introduced in order to reduce the partial pressure of the vapour. It was desired to reduce the partial pressure to the greatest possible extent in these experiments, but at the same time the introduction of too large a volume of nitrogen leads to experimental difficulties, and for these reasons a ratio of 2 vols. of nitrogen to 1 of vapour was chosen.

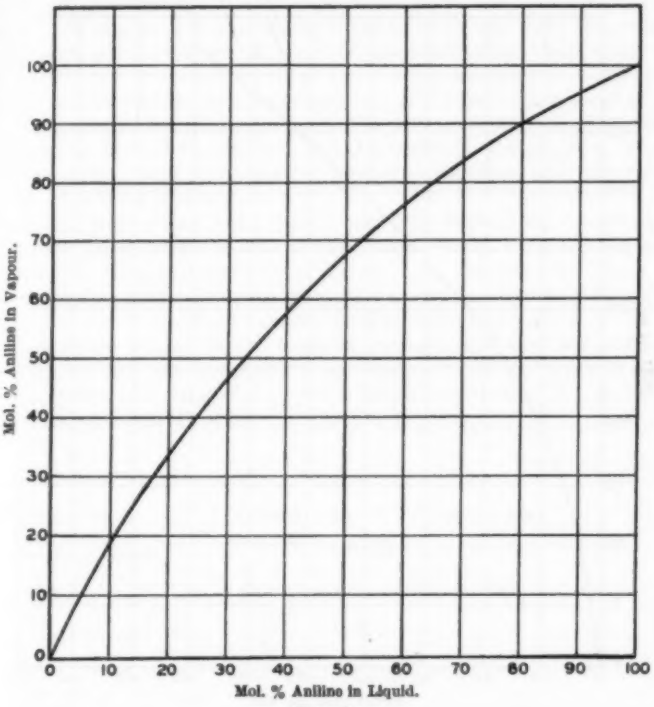


FIG. 4.

NITROBENZENE–ANILINE EQUILIBRIUM CURVE AT 253 MM. PRESS.

Description of Apparatus.—The first set of experiments were carried out using a glass still and column. The total capacity of the still was 5 litres, and the charge 2 litres. The column was 2 in. in diameter, and was packed with ¼-in. Lessing rings for a height of 36 in. The column was electrically lagged by a winding placed on a sheet-iron cylinder 2½ in. in diameter, the space between the cylinder and the column being filled with powdered asbestos. Two surface couples, placed 9 in. from the top and bottom of the iron sheath, measured its temperature, and so allowed the heat input into the winding to be accurately adjusted. The bottom half of the still was embedded in a box of lagging, and the top half was lagged electrically, the still being heated electrically.

A total condenser made of brass was placed on top of the column. The condensate from this condenser was collected in a small gallery, from which it could be run out into a receiver through a glandless cock. The excess of condensate spilled over from the gallery to provide reflux.

The temperature in the still and at the column head was measured by thermocouples, the one at the top being provided with a radiation shield.

A rotary oil-pump was used to evacuate the still, the pressure being

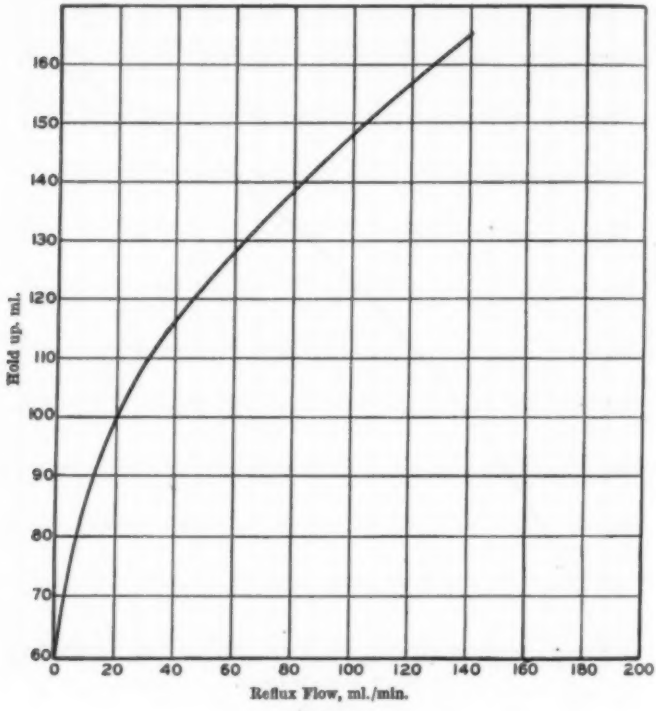


FIG. 5.

HOLD-UP IN LESSING RING PACKED COLUMN.

controlled by means of a leak. The pressure was measured on a mercury manometer.

The heat loss for the various parts of the apparatus was first accurately determined.

The hold-up in the condenser was found to be 16 ml., whilst that in the column for various rates of liquid reflux is shown in Fig. 5. Subsequently a metal still and column were constructed, the column diameter being $1\frac{7}{8}$ in. and the packed height 35 in. In other respects it was the same as the glass still already described, except that the opportunity was taken to guard more effectively against heat loss from the body of the still.

Experimental Procedure.—Two litres of a mixture of appropriate composition (roughly 15–20 per cent. aniline by volume) were charged to the still, and the heating current was switched on. The pressure on the still was regulated to give that desired, either 10 mm. or 253 mm. of mercury. The column was operated under total reflux for 1 hr., and the draw-off cock was then opened to produce distillate at such a rate as to give the desired reflux ratio. After 100 ml. had been taken off, the distillation was stopped and the liquid retained in the column head was collected for analysis. A sample was immediately taken from the still, the bulk of the hold-up being retained in the columns until after the sample was withdrawn.

The heat input to the still was measured, and from a knowledge of this and of the heat loss the net heat input to the mixture was obtained. Knowing the latent heat of the mixture (see Appendix I), the quantity passing into the column could be calculated, and this, together with the rate of take-off, gave the reflux ratio.

Normally, high reflux ratios (about 15 : 1 or higher) were used, since in this way inaccuracies in the measurement would have only a small effect on the estimated number of plates; but, in order to check the accuracy of the method, an experiment was carried out at 7 : 1 reflux-ratio, which showed that the estimated reflux-ratio was correct.

The refractive indices of the samples from the still and the overhead were measured and the composition was obtained. The number of plates was then estimated using McCabe and Thiele's method. The results of a typical experiment are given:

Experiment No. 2 (glass still).

Distillation rate	0·8 ml./min. = 0·83 grm./min.
Analysis of overhead	$\frac{\mu\ 15{\cdot}6}{D} = 1{\cdot}5823$
	Mol. per cent. aniline = 88
,, ,, still content	$\frac{\mu\ 15{\cdot}6}{D} = 1{\cdot}5572$
	Mol. per cent. aniline = 11·5
Mean mol. wt. of overhead	= 97
∴ Mols. taken off/min.	= 0·00855
Heat input to still	= 5·6 amps. × 23 volts = 129 watts.
Heat loss	8 watts
Net heat input	121 watts
Mean mol. latent heat	56,400 joules

$$\therefore \text{No. of mols. entering column per min.} = \frac{121 \times 60}{56{,}400} = 0{\cdot}1307$$

$$\therefore \text{reflux ratio} = \frac{0{\cdot}1307 - 0{\cdot}0086}{0{\cdot}00855} = 14{\cdot}3 : 1$$

Total No. of plates	= 6·8
Still effect	1
No. of plates in column	= 5·8

In the experiments in which nitrogen was introduced as a diluent, the required volume of dried gas was preheated to the still temperature and bubbled through the liquid in the still. The column was operated at a total pressure of 760 mm. The volume of nitrogen was measured on a carefully calibrated flowmeter. Extra condensing arrangements were installed, and the gas was cooled to 0° C. before leaving the apparatus. All condensate was returned to the column as reflux, so as to avoid introducing any ambiguity owing to the unknown fractionation produced by a partial condenser. In other respects the experiments were conducted in the same way as those already described.

Experimental Results.—The experiments made on both the glass and iron columns were:

(1) Estimation of H.E.T.P. at 10 mm. pressure.
(2) ,, ,, ,, ,, 253 ,, ,,
(3) ,, ,, ,, ,, 760 ,, ,, using 50–60 per cent. nitrogen as diluent.

The velocity up the column was varied both in the experiments at 10 mm. and in those at 253 mm., the highest mass velocity being roughly three times the lowest. Three heights of packing were investigated in the iron column, namely 23 in., 29 in., and 35 in., in experiments at high and low velocities at 253 mm.

The experimental results are shown in Tables 1 and 2, together with estimated values for the viscosity of the vapour and for the diffusion coefficient. There are no experimental figures available for the viscosity of aniline or nitrobenzene vapour. In order to obtain a value for the viscosity which could be used in subsequent calculations, it was assumed that the aniline–nitrobenzene mixtures have a viscosity equal to that of a hydrocarbon of the same molecular weight. The viscosity of the nitrogen–nitrobenzene–aniline mixture was calculated using the estimated viscosity for nitrobenzene–aniline, by the modified Kuenen's formula.

It has been shown that for turbulent flow in a column

$$H \propto \frac{vD^2}{\Delta\left(\frac{vD\rho}{\eta}\right)^{0\cdot 8}}$$

H = H.E.T.P.
D = diameter of packing.
v = linear velocity of vapour up column.
Δ = diffusion coefficient.
ρ = density of vapour.
η = viscosity of vapour.

The experimental results were therefore used to obtain values for the function $\frac{H\Delta}{v}$, and this is shown in Figs. 6 and 7 plotted against $\frac{vD\rho}{\eta}$, log. scales being used.

The value of "D" used was the diameter of the rings (0·63 cm.), and for this reason it appears that the value of the Reynolds number is lower than is necessary for turbulence to exist. The values of $\frac{vD\rho}{\eta}$ in the unpacked

TABLE 1.
Glass Still.

Expt. No.	Press. mm.	Mol. % aniline. Top.	Mol. % aniline. Bot.	Dist. rate mol./min.	Rate up col. mol./ min.	Reflux ratio.	No. of Plates.	H.E.T.P. cm.	Mean temp. °C.	Vel. cms./ sec.	Δ^*.	$\frac{\rho}{\times 10^4}$.	$\frac{\eta}{\times 10^4}$.	$\frac{vD\rho}{\eta}$.	$\frac{H\Delta}{v}$.	% dil.
1	10	97	48·5	0·00987	0·1225	11·4	4·6	19·9	71	222	0·153	0·047	64	103	0·137	
2	8	88	11·5	0·00855	0·1307	14·3	5·8	15·8	71	296	0·179	0·04	64	117	0·0955	
3	9	92·2	23	0·0152	0·1202	6·9	6·0	15·25	72	250	0·160	0·045	64	111	0·0975	
4	9·5	83·2	14·8	0·00925	0·1202	11·9	6·5	14·1	72	230	0·149	0·048	64	109	0·0915	
5	9·25	91	22·5	0·02385	0·438	17·4	4·7	19·5	77	875	0·162	0·045	65	382	0·0362	38% N_2
6	760	83·3	14·6	0·0129	0·2990	22·2	4·0	22·9	169	14·4	0·040	2·14	94	203	0·0635	
7	380	91	14·5	0·0101	0·2962	28·4	5·3	17·3	169	18·2	0·063	1·48	83	204	0·060	
8	760	89·8	24·5	0·00497	0·1368	26·5	3·7	24·7	150	9·7	0·0466	1·7	125·5	90	0·119	58·5% N_2
9	253·5	99·5	25·2	0·0384	0·1514	38·5	8·3	11·05	150	13·3	0·086	1·03	79	109	0·0715	

* The ratio $\frac{\eta}{\rho\Delta}$ should be constant and equal to 1·34 for all cases except those in which diluent gas is employed. In order to obtain some sort of consistency between values of Δ with and without diluent, a formula has been used which makes the above ratio 1·12 for pure vapour. The only effect on the results as plotted is to displace the points and lines uniformly.

TABLE 2.

Iron Still.

Expt. No.	Press. mm.	Mol. % aniline. Top.	Mol. % aniline. Bot.	Dist. rate mol./ min.	Rate up col. mol./ min.	Reflux ratio.	No. of Plates.	H.E.T.P. cm.	Mean temp. °C.	Vel. cms./ sec.	Δ.	$\rho \times 10^3$.	$\eta \times 10^6$.	$\frac{vD\rho}{\eta}$.	$\frac{H\Delta}{v}$.	% dil.
							23-in. Rings.									
1	253·5	85	11·5	0·00368	0·158	17·2	5·1	12·45	150	15·5	0·086	1·03	79	127	0·069	
2	253·5	87·5	11	0·00679	0·157	22·1	5·2	12·2	150	15·4	0·086	1·03	79	127	0·068	
3	253·5	87·5	13	0·01047	0·497	46·5	4·5	14·1	150	48·8	0·086	1·03	79	400	0·0248	
							29-in. Rings.									
4	253·5	90	9·5	0·0083	0·157	17·9	6·2	11·9	150	15·4	0·086	1·03	79	127	0·0665	
5	253·5	87·5	7·3	0·00614	0·158	24·75	6·7	11·0	150	15·5	0·086	1·03	79	127	0·061	
6	253·5	79·5	7	0·0108	0·497	45	5·0	14·9	150	48·8	0·086	1·03	79	400	0·0262	
							35-in. Rings.									
7	253·5	92	7·5	0·0108	0·498	45·2	6·4	13·9	150	49	0·086	1·03	79	401	0·0244	
8	253·5	92·5	7·1	0·00865	0·157	16·95	8·5	10·45	150	15·4	0·086	1·03	79	127	0·068	
9	9·5	88·2	4·9	0·0101	0·21	19·8	6·3	14·1	76	485	0·162	0·045	65	202	0·047	
10	9·8	89·8	8·0	0·00860	0·202	22·5	6·9	12·9	76	450	0·157	0·0465	65	194	0·045	
11	760	87·9	13	0·00555	0·184	33	3·9	22·8	150	15·4	0·0468	1·72	124·5	134	0·069	56·5% N_2
12	760	95·5	13·25	0·00505	0·167	32	5·9	15·1	145	14·3	0·0495	1·70	125·5	122	0·0523	57·5% N_2
13	760	95	12	0·0055	0·124	21·5	6·4	13·9	140	12·9	0·0545	1·54	137	91·5	0·059	67% N_2

column range from 800 to 3,200, and it is unreasonable to suppose that rings tumbled into a column haphazard will tend to stabilise the flow, so that it is legitimate to say that turbulence exists in the column.

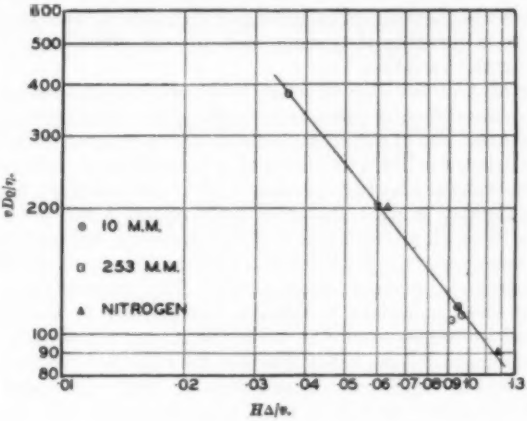


FIG. 6.

CORRELATION OF EXPERIMENTAL RESULTS: GLASS STILL.

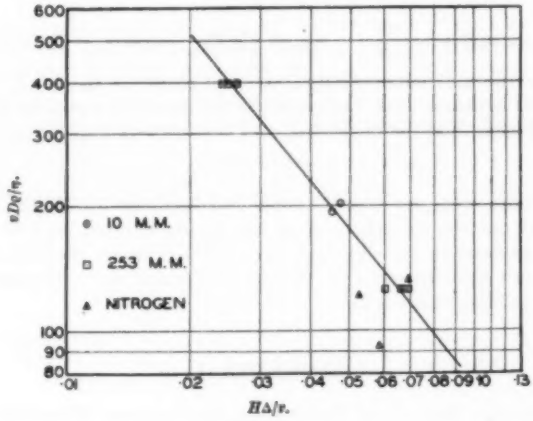


FIG. 7.

CORRELATION OF EXPERIMENTAL RESULTS: IRON STILL.

Experiments 1 and 9 in the glass still are untrustworthy, on account of the high percentage of aniline in the product, and the points have not been plotted on the graph.

It will be noticed that the points for the experiments at 10 mm. and 253 mm. fall on two straight lines, one for each still. These lines indicate

that the above formula correctly interprets the experimental results over the range of variables used here.

The difference between the two lines indicates a difference in efficiency between the two stills, which is due probably to slight variations in the way in which the Lessing rings arranged themselves, and in reflux distribution. It is possible that some sort of end effect may have been responsible for the variation.

The value of Δ in the case of a mixture such as nitrobenzene–aniline, in which the two diffusing gases are of nearly the same molecular weight and have the same size of molecule, is directly proportional to the viscosity, and if the substitution for Δ in terms of η is made in the above formula, it can be seen that the effect of viscosity is $\eta^{0\cdot2}$. If, therefore, the assumed value of η is slightly in error, the error in the equation will not be great.

In the case in which nitrogen is introduced, however, the relation between Δ and η no longer holds. Both these quantities must be calculated from equations based on certain assumptions. The experimental evidence for checking these equations is meagre, particularly in the case of the viscosity, and in consequence the values of Δ and η are open to doubt. It is not possible, therefore, to say whether the fact that the cases in which nitrogen is used as a diluent do not give as good agreement with the equation as the others is due to some imperfection in the theory or to errors involved in calculating Δ and η.

It is possible that the thickness of the streamline layer is dependent on other functions besides $\frac{vD\rho}{\eta}$. In the case of heat transfer, for instance, the thickness varies as $\left(\frac{\eta C}{K}\right)^{0\cdot4}$, where η is the viscosity, C the specific heat, and K the thermal conductivity. It was assumed in the development of the above equation that variations in this term, or a similar one applicable to diffusion, may be neglected, and this neglect may have introduced some error.

The authors wish to express their indebtedness to R. A. Chisholm, who carried out the experiments on the 8-mm. column, and to W. H. S. Bell, who assisted in carrying out the distillations on the 2-in. columns; and to thank the Directors of the Anglo-Persian Oil Company for permission to publish this work.

APPENDIX I.

Latent Heats of Nitrobenzene–Aniline Mixtures.

The molal latent heats of nitrobenzene and aniline at 1 atmosphere (from the International Critical Tables) are :—

Nitrobenzene	40,700 joules.
Aniline	40,400 ,,

The molal latent heats are almost identical.

For lower pressures the values were calculated from the vapour-pressure

data in the International Critical Tables, and the following values were obtained:

Nitrobenzene

112—209° C. mean molal latent heat = 48,955 joules
80—100° C. „ „ „ „ = 55,900 „

Aniline

145—185° C. „ „ „ „ = 45,952 „
60— 80° C. „ „ „ „ = 56,100 „

From these figures and the experimental values at 1 atmosphere graphs were drawn, and from these the following estimated molal latent heats were obtained:

Pressure mm. Hg.	Nitrobenzene joules/mol.	Aniline joules/mol.
10	56,500	56,300
253	49,000	48,000
380	47,100	46,000

Mean values of 56,400, 48,500 and 46,550 joules/gram were used in the calculations.

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A CONTRIBUTION TO THE STUDY OF OILFIELD WATER ANALYSIS. PART V. THE ESTIMATION OF POTASSIUM.

By Wilfred Richard Wiggins, B.Sc., and Charles Edmund Wood, M.Sc., A.I.C. (Member).

SYNOPSIS.

1. Using sodium-6-chloro-5-nitrotoluene-3-sulphonate as precipitating reagent for potassium, a rapid colorimetric and two volumetric methods for the estimation of potassium have been developed.

2. In the colorimetric method the precipitated potassium employed is reduced, diazotised, and coupled with R-salt to produce a soluble red dye, the intensity of colour being proportional to the amount of potassium present; this method is rapid, suited for routine laboratory use, but is not of great accuracy.

3. In the volumetric methods the precipitated potassium salt is reduced with stannous chloride or titanous chloride and excess reducing agent determined. With titanous chloride for solutions containing 25–35 grm. KCl per litre, the results show highest accuracy.

4. Ammonia should not be present; calcium and magnesium cause only slight positive errors. No preliminary separation of other metals is necessary. Estimation of potassium can be completed in 2–3 hours.

Sodium and potassium are the alkalies most frequently encountered in underground waters. The total alkalies are generally returned in analyses either as sodium [7, 9] or as Na + K,[3] without indication of the amount of potassium, and further the figures recorded are not direct estimations, but are the values equivalent to the difference between the metallic ions determined and the acidic radicals. Since simple potassium salts are soluble, it is to be expected that potassium would occur in all waters in intimate contact with sedimentary strata. The presence of potassium in mineral waters is widely recorded.[6, 2]

The methods usually adopted for the estimation of potassium in the presence of sodium involve the use of perchloric acid, sodium cobaltinitrite, and chloroplatinic acid which are gravimetric procedures, the second having been modified into a volumetric nitrite estimation.[5, 1] The object of this investigation was to develop a simple and rapid method suitable for routine analysis of underground waters; the results of such analyses would undoubtedly throw light on the hypothetical ionic combinations and facilitate accurate correlation of mineral waters.

H. Davies and W. Davies [4] pointed out that the insolubility of potassium-6-chloro-5-nitrometatoluene sulphonate compared favourably with potassium perchlorate and potassium chloroplatinate, whereas the corresponding sodium salt was appreciably soluble (10–12 per cent.) in water. These authors adopted a gravimetric procedure using the sodium salt as precipitating reagent. The time taken by this gravimetric method is, however, too lengthy for routine laboratory adoption. Owing to the easy solubility of the potassium salt, the use of 2 : 4-dinitrophenol is not suit-

able for quantitative work, although it has been suggested for the qualitative detection of potassium.[8]

The following three methods, I colorimetric, II and III volumetric, based on the insolubility of potassium 5-nitro-6-chlorotoluene-3-sulphonate and the reduction of the nitro-group, have been investigated and proved particularly satisfactory over certain potassium concentration ranges. Owing to the number of different groups in the benzene nucleus, there appears to be a wide choice on which to base a volumetric method, but the chlorine is firmly fixed, and the estimation of the sulphonic acid group presents difficulty.

I. *Colorimetric Determination.*—The potassium salt precipitated in a definite reaction volume was dissolved in a specified quantity of hot water acidified with dilute sulphuric acid. The solution, after passage through a Jones reductor, was diazotised and coupled with alkaline R-salt. The colour produced was evaluated by comparison with standard slides in a Lovibond tintometer or compared with standard solutions in Nessler glasses.

Experimental Procedure.—To 5 ml. KCl solution and 5 ml. distilled water, 25 ml. of sodium-5-nitro-6-chlorotoluene-3-sulphonate (10 per cent. solution) were added; after stirring, the mixture was kept for 1 hour at 15° C. The precipitate was separated in a crucible porosity B2, washed with 10 ml. water, and dissolved in hot water (for precipitates up to 10 grm. KCl per litre, 100 ml. water were used and *pro rata*). An aliquot portion containing 15–25 mgrm. potassium after acidification with 15 ml. H_2SO_4 (25 per cent. by weight) was passed through a Jones' reductor; the reduced solution was diazotised with 10 ml. of 0·2*N*-sodium nitrite solution, then added to 50 ml. R-salt solution (0·6 per cent. salt in 10 per cent. NaOH), and the mixture was made up to 250 ml. with water, any precipitated zinc hydroxide being filtered off. The colour intensity was measured in a $\frac{1}{16}$-in. cell with Lovibond red and yellow slides which had been calibrated previously against standard amounts of the diazotised and coupled potassium salt. A direct comparison against standard amounts of potassium was effected also in Nessler glasses.

TABLE I.

	Tintometer.				Nessler Glasses.		
KCl per litre .	4·9989	10·0006	20·0015	40·0013	4·9989	10·0006	20·0015
K grm. present .	0·0131	0·0263	0·0526	0·1051	0·0131	0·0263	0·0526
Colour—red units for $\frac{1}{16}$" cell solution .	7·1	26·0	21·85 *	21·75 †	—	—	—
K grm. estimated	0·0063	0·0230	0·0483	0·0963	0·0066	0·0213	0·0485
Error . .	−0·0068	−0·0033	−0·0043	−0·0088	−0·0065	−0·0050	−0·0041

* Precipitate dissolved in 250 ml. water, 100 ml. taken, reduced, diazotised, etc.
† Precipitate dissolved in 500 ml. water, 100 ml. taken, reduced, diazotised, etc.

Table I indicates that the method is fairly accurate for KCl concentrations of 10–40 grm. per litre, but breaks down below 10 grm. KCl per litre on account of incomplete precipitation of the potassium nitrochloro-

sulphonate. The Lovibond tintometer and Nessler Glass methods give comparable results.

The effect of diluting the dye was examined, and it was found that potassium concentration and colour intensity (units of red) followed a linear relationship for the concentrations recorded. The alkalinity of the R-salt solution had a marked effect on the colour intensity, and, in order to obtain concordant results, it was necessary to keep the acidity of the reduced solution and the alkalinity of the R-salt constant.

II. *Volumetric Procedure. Reduction of the Nitro-group with Excess of Stannous Chloride.*—The precipitate obtained as described above was transferred with the aid of 50 ml. of hot water to a flask fitted up so that the reduction and titration could be carried out in an atmosphere of CO_2; a large excess (20 ml. approx.) 0·5*N*-$SnCl_2$ was added, the whole heated for ½ hour, cooled and titrated with 0·1*N*-iodine solution.

TABLE II.

KCl grm. per litre . . .	10·0006	20·0015	30·0020	40·0013
K grm. present . . .	0·0263	0·0526	0·0789	0·1051
K grm. found. . . .	0·0239	0·0488	0·0733	0·0959
Error	−0·0024	−0·0038	−0·0056	−0·0092

Time of standing was 1 hour at temperature 15°, and concentration of the precipitating reagent was 8 per cent. The results are recorded in Table II. The negative error cannot be wholly due to incomplete precipitation of the potassium salt, as it is approximately constant throughout the concentration range. It was inferred, therefore, that incomplete reduction by $SnCl_2$ contributed to this error. Even when time of reduction and excess of stannous chloride over the volume recorded above were increased, a similar negative error resulted. In addition, reduction of weighed amounts of dry potassium salt gave a similar error. All experiments throughout this paper were done at least in quadruplicate.

III. *Volumetric. Reduction of the Nitro-group with Excess of Titanous Chloride.*—A procedure similar to that described for stannous chloride was adopted. The precipitate of the potassium salt obtained as described above was washed with 5 ml. water, transferred with the aid of 50 ml. hot water to a conical flask, a 10 ml. excess approximately titanous chloride added and the mixture heated nearly to boiling for 10 minutes. The excess of reducing agent was titrated in the cold with iron alum solution in the usual way. The whole operation was performed in an atmosphere of carbon dioxide.

TABLE III.

KCl grm. per litre . . .	10·0006	20·0013	30·0020	40·0013
K grm. present . . .	0·0263	0·0526	0·0789	0·1051
K grm. found . . .	0·0243	0·0495	0·0774	0·1116
Error	−0·0020	−0·0031	−0·0015	+0·0065

Table III shows that as the potassium chloride concentration increases from 10 to 40 grm. per litre, the negative error due to non-precipitation decreases, and at the higher concentration is more than balanced by the

positive error due to occlusion of the precipitating reagent. This method gives reasonably accurate results over the range 10–40 grm. KCl per litre, and very accurate results for 25–35 grm. KCl per litre. The negative errors obtained for lower concentrations may be accounted for partly by solubility of the potassium salt (4 mgrm. K per 10 ml. water at 15° C.) in the wash water used. The percentage errors plotted against concentrations lie on a smooth curve which crosses the axis (zero error) at a concentration of 33 grm. KCl approximately per litre.

The effects on precipitation by calcium and magnesium ions were investigated using titanous chloride.

TABLE IV.

KCl grm. per litre	20·0015	20·0015	20·0015
K grm. present	0·0526	0·0526	0·0526
K grm. found	0·0495	0·0510	0·0523
Magnesium grm. present	—	0·0326	—
Calcium grm. present	—	—	0·09152
Error	−0·0031	−0·0016	−0·0003

The results in Table IV show that Ca and Mg, when present in maximum concentrations occurring in ordinary underground waters, cause only a slight *positive* error (when compared with results obtained in the absence of these metals), *i.e.* the *negative* error due to non-precipitation is decreased by the presence of these metallic ions.

Ammonia, on account of the extremely low solubility of ammonium 5-nitro-6-chlorotoluene-3-sulphonate, should not be present. Ammonia, however, does not occur in any appreciable concentration in underground waters.

Difficulty was encountered in obtaining specimens of sodium nitrochlorotoluenesulphonate of constant composition; 25 ml. of a 10 per cent. solution of the salt with 5 ml. KCl, concentration 10 grm. per litre, and 5 ml. water should form a dense precipitate in 2–3 minutes.

Besides simplicity and accuracy, the method gives quick results. No preliminary separation of other metals is necessary, and potassium can be estimated in duplicate in 2–3 hours. The use of this method is not necessarily confined to water analysis.

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SOME VISCOMETRIC MEASUREMENTS ON CLAY SUSPENSIONS.

By G. D. Hobson, B.Sc. (Student).*

In connection with a number of problems, mud or clay-water systems have been examined in viscometers of various types. The ceramist, desiring some means of assessing the plasticity of clays, found that the behaviour of diluted slips in a viscometer bore relations to the complex property of plasticity which were probably closer than such properties as dye and water-vapour absorption, etc. To the engineer the viscous properties of these systems are of interest, in that a knowledge of them is essential in the construction of pumps and pipe-lines used for conveying these materials. The oil-field engineer finds in the viscometry of mud-water systems a method of determining, and a means of controlling, some of the desirable properties for clay-water suspensions used in drilling.

The following is an indication of some of the work that has been done, of the methods used and the results obtained.

Oscillating Disc Viscometer.

The Coulomb oscillating disc viscometer was used by Bleininger.[1] From the ratio of successive amplitudes, R, under given conditions, and T, the period of oscillation, he calculated a factor K, which is proportional to the viscosity as follows :—

$$R = e^{-TK}$$

Barr [2] points out a number of experimental difficulties in the method, and that, as a consequence of inexactitudes in the theoretical equations, at least three instrumental constants must be determined even for relative measurements. Bleininger states that the apparatus is applicable only to fine-grained materials, and in concentrations not exceeding 15 per cent. He found a slight minimum in his viscosity-concentration curves at about 3 per cent.

Capillary Tube Viscometers.

Capillary viscometers have been used widely in these measurements on clay suspensions. The Mariotte bottle type of apparatus has been used by Mellor, Green and Baugh,[3] and by Back [4] and Simonis. The former workers measured the time of efflux of a definite volume of the fluid through a capillary of bore 2–3 mm., but their data indicate that the Reynolds number for the flow would be exceptionally high for the more fluid suspensions. Using a composite slip they found that :—

(1) Small additions of the following substances make the slip more fluid, larger additions stiffen it : sodium carbonate and sulphide; fusion mixture, potassium carbonate, sulphate, bisulphate, hydroxide and nitrate; tannin and gallic acid.

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(2) Small amounts of copper sulphate, potash alum and dilute ammonia thicken, whilst larger amounts make the slip more fluid.

(3) Sulphates of magnesium, mercury and sodium; sodium sulphite, acetate, chloride and hypophosphate; ammonium gallate, hydrochloric acid and water glass make the slip thinner. These may fall into group I at higher concentrations.

(4) Grape sugar, humic acid, borax, ammonium chloride and urate; calcium chloride and sulphate; aniline, ethylamine and methylamine make the slip stiffer. These substances may fall into classes 1 or 2 if greater or lesser amounts are used.

(5) Some substances have no appreciable effect on the slip—*e.g.* alcohol.

Simonis, using a 2 mm. aperture and different constant applied pressures, found a non-linear relationship between time of flow and driving head, but experienced difficulties in working with thick slips.

In order to get a slip of uniform viscosity for all tests, Back [4] found it necessary to dry the clay for 3½ hours at 110° C. When heated for only 2 hours there was a marked increase in viscosity on standing. The effect of electrolytes on the slips was also dependent on the time of drying, as well as on the actual clay used, and the action of caustic soda showed a time effect possibly due to the absorption of carbon dioxide.

An Ostwald capillary viscometer appears to have been used by Bingham and Durham [5] in their work on suspensions of china-clay and infusorial earth. They conclude that finely divided substances in suspension depress the fluidity of the liquids in which they are suspended by amounts which are directly proportional to the volume of suspended solid. (Einstein's equation [6] indicates that the increase in *viscosity* is proportional to the volume of suspended solid.) The depression is such that a zero value of fluidity is reached at a definite, but small percentage by volume, of the solid. The composition for zero fluidity is independent of the temperature and the apparatus used. It appears to demarcate viscous from plastic flow, and can be changed by the addition of small quantities of electrolytes.

In a further investigation of china-clay suspensions, Bingham [7] used an efflux type of viscometer or plastometer. He examined more concentrated suspensions than in the previous work, using capillaries of different lengths and diameters, and varying the driving head of air under pressure. When the rate of flow was plotted against the pressure, he found that "for a certain medium range of pressures the volume of flow is quite accurately represented by :—

$$v = K(P - f),$$

where f is the friction constant—the graphical intercept on the pressure axis considered as the force necessary to begin flow." This constant was independent of the capillary, and unchanged when the temperature was raised from 25° C. to 40° C. At high-pressure gradients in some capillaries the flow suddenly increased. He attributed this to slippage. Flow may also occur at pressures less than the intercept on the pressure axis, which flow he considered due to seepage. The change in mobility (K — the slope of the flow curve) with rise in temperature is almost exactly the same as the change in fluidity of the suspending medium. The friction constant appears at the concentration at which the fluidity of the china-clay sus-

pension becomes zero, and then increases rapidly and in a linear manner with increase in concentration.

The Bingham type of plastometer has also been used by Hall,[8, 9] and by Wilson and Hall.[10] The latter used caustic soda and hydrochloric acid to examine the effect of *p*H value on mobility and yield value (Table 1), and also deduced from the effects of adding sand to the clay slips that it does not hold nearly so much water as does clay. Hall [9] found that "the consistency of a clay slip changes during the first two days, probably due to the swelling of gel colloids, and more on the first day than in later periods." Hence all the determinations with one capillary must be made in one day. He suggests that the deviations of experimental data from the theoretical curves based on Bingham's hypothesis are due to end effects. His dilute suspensions gave the break observed by Bingham at high rates of shear, and he finds that the slope of the $\frac{4V}{\pi R^3 T} - \frac{PR}{2L}$ curves (the flow curves) is greater the narrower the capillary.

TABLE 1.

Hydrogen ion concentration.	Mobility as percentage of value in neutral water.	Yield value in arbitrary units.
10^{-3}	91%	339
10^{-4}	95%	321
10^{-5}	98%	306
10^{-6}	99%	297
10^{-7}	101%	283
10^{-8}	106%	238
10^{-9}	111%	192
10^{-10}	120%	51

From the data of Wilson and Hall.

Davis [11] finds the action of tannic acid on clay slips to be slow, increasing the viscosity at low and high concentrations, but decreasing it at intermediate concentrations of acid. It gave excellent suspension of the clay particles even in dilute slips. Gallic acid had little effect, and both sodium carbonate and silicate reduced the viscosity at quite low concentrations, but the latter gave only poor suspension.

A form of the burette consistometer was used by Cooke.[12] The burette and capillary were set in a condenser jacket through which water at a constant temperature was circulated. The average pressure (arithmetic mean) and average rate of flow for each 5 c.c.s. were plotted, and from the curve the mobility and yield value were determined. A rise in temperature from 14° C. to 35° C. increased the mobility 60 per cent. (the fluidity of water changes by about 62 per cent. over that range) without changing the yield value.

If, in using a burette consistometer, the flow is timed over large linear intervals, it is no longer sufficiently accurate to use the arithmetic mean as the average head, especially at the lower readings. Then the Meissner formula should be applied for true fluids, since the kinetic energy correction will usually be made small, in which case the complex Dryden equation will be unnecessary. But kinetic energy corrections may be necessary at the initial high rates of flow. If the interval timed at the lower heads is

reduced, the arithmetic mean value approaches more closely to that calculated from the Meissner equation.

In the case of a non-Newtonian fluid, the Meissner equation is not correct. An approximate formula for a plastic material is derivable from the shortened form of Buckingham's equation. This can be applied in conjunction with an independent determination of the stress intercept involved, or by a method of successive approximations, but has weaknesses at the lowest heads.

Barr [13] notes that " if the apparent viscosity is affected by working, those types of apparatus are to be preferred in which results for different rates of shear are obtained in one continuous operation, as in the burette consistometer." Scott Blair and Crowther [14] observed that the results of the first passage through the capillary in their apparatus were often irregular, but measurements with subsequent shearings were consistent, and the number of shearings had no effect on the flow curve. But Demolon and Barbier,[15] working with suspensions treated with electrolytes, found that passing them through a capillary several times decreased the time of flow, whilst stirring for 2 hours brought it to a constant value. It is possible that this is a matter of the action of the electrolyte on the suspension requiring time to become complete, for their procedure was to measure the " viscosity " 30 seconds after the addition of the electrolyte.

Using a brick-earth, suitably treating it with hydrochloric acid and soda, washing and dialysing, Demolon and Barbier obtained a suspension with a fixed " viscosity." Its " viscosity "–concentration curve was hyperbolic, the " viscosity " increasing very rapidly above 55 grms./litre, at which concentration rigidity first appeared. Working with a concentration of 20 grms./litre they found that the addition of electrolytes increased the " viscosity " rapidly to a maximum, after which it fell off slowly with further additions of electrolyte. No single point seemed to mark the beginning of flocculation; the increase in " viscosity " was shown for concentrations below those which gave visible precipitation, and continued for some time after. Nitrates and chlorides had similar effects, but sulphates always had less effect, and of the metallic ions sodium was the weakest.

The mechanism of the flow of soil and clay pastes in capillaries has been studied by Crowther, Keen, Schofield and Scott Blair in a series of papers. Their apparatus consisted of twin bulbs connected by a capillary, and by the manipulation of cocks air pressure could be applied to drive the paste from one bulb to the other and back again. The rate of flow of the paste was measured by the displacement of air through a flow-meter, and hydrostatic head corrections were avoided by tilting the apparatus to keep the top of the paste in the two bulbs at the same level. Concentrations of clay ranging from less than 5 per cent. to more than 50 per cent. were examined.

From their flow curves (rate of flow plotted against pressure) they distinguish five stages :—

I. The paste does not flow until a certain pressure is reached.

II. The paste moves as a rigid cylindrical plug through a thin envelope of the fluid which adheres both to the wall of the tube and to the plug. Over this range the rate of flow increases linearly with the applied pressure.

III. The diameter of the plug decreases. In the annular space round the plug the paste has stream-line flow. The volume of flow increases at a faster rate than the pressure applied. The diameter of the plug decreases as the pressure increases, and the flow curve rapidly approaches linearity.

IV. Here the flow is so near streamline throughout that the error involved in assuming linearity between volume of flow and pressure becomes negligible.[16]

V. Dilute pastes show a curvature towards the pressure axis at the highest rates of flow—this is due to the fact that a kinetic energy correction is not applied—there may also be turbulence in some cases.[17]

These authors discuss the simple mathematical relationships applicable to the different stages[14] and the conditions under which they fail, and suggest that the most likely explanation of stage I is the presence of a fluid layer adjacent to the wall, across which bonds exist which are broken down on the attainment of a certain critical shearing stress. They demonstrate the essential difference of the two linear portions of the flow curve, II and IV, by showing that the first is seriously affected by etching the walls of the capillary, but not the second.

Assuming the Bingham hypothesis that a critical shearing stress f is necessary before flow can begin, the following equation is derived embracing stages I, II, III and IV[18]:—

$$V = \frac{\pi R^4}{8l\eta'}\left(P - \frac{4}{3}p + \frac{p^4}{3P^3}\right) + \frac{\pi R^3 \epsilon\phi(P - a)}{2l}$$

R = radius of capillary; l = length of capillary; P = applied pressure; $p = \frac{2lf}{R}$; a = pressure at the beginning of stage II; V = rate of flow; ϵ = the thickness, and ϕ = the fluidity of the lubricating layer on which slip occurs in stage II. This equation differs from that derived by Buckingham only in the inclusion of the factor a in the slip term, in order to account for stage I.

When Scott Blair and Crowther[19] plotted $\frac{V}{\pi R^3}$ against $\frac{PR}{2L}$, their flow curves fell into two groups, one of which gave points on a straight line for a single capillary, the slope of this line being greater the narrower the capillary. The other had points showing no regular trend with change of radius. A systematic spreading of the curves for different capillary radii is an indication of the presence of a σ_0 factor—a factor which they believe to represent exceptional mobility in the material near the capillary wall, but not actual slip at the wall. They give a simple geometrical method by which the value of this factor may be determined, and point out that whilst the alignment of laminar particles near the wall of a capillary might be expected to give excessive fluidity in that region, this phenomenon is not confined to suspensions of laminar particles. Its value is zero for pure water, but rapidly increases up to a point corresponding roughly with the concentration at which the suspension begins to show a shearing strength. It passes a maximum, and finally approaches zero just as the shearing strength becomes too high to make further measurements practicable.[17]

Schofield [20] gives a geometrical exposition of the derivation of the flow relationships of these suspensions.

The Marsh funnel viscometer is an inverted cone of specified dimensions, with a drilled copper tube in the apex,[21, 22] and this has been modified by Strong,[23] who added a column 120 cm. long. "The plasticities of muds are roughly compared by means of the efflux in c.c.s./sec. with an orifice pressure of 120 grms./cm.,^{2} which pressure with this instrument is sufficient to give a steady flow for all muds used in normal drilling circulation." The Trinidad I.P.T. viscometer is a cylindrical vessel with a bored tube of given dimensions in the bottom.[24]

Concentric Cylinder Rotating Viscometers.

Bleininger and Brown [25] examined clay slips in a Stormer viscometer fitted with paddles and driven by a 200-grm. weight. Later Bleininger and Clark [26] used the same instrument when rotated by an electromagnetic device. It is pointed out that the instrument is in no way absolute, but has the advantage that the slip is stirred thoroughly during the measurement, so preventing settling. However, the air and water constants are liable to fluctuate.

The Stormer viscometer has been tested by Rigg and Carpenter,[27] and by Higgins and Pitman.[28] The former workers have doubts as to the value of the instrument, and would limit its use to the mere comparison of liquids the difference in fluidity of which is small and will not require a change in the driving weight. The latter workers report more favourably, and suggest that its most useful range is 20–500 centipoises using a 150-grm. weight.

The calibration of the Stormer viscometer to obtain weight–viscosity–rate of revolution curves is described in Drilling Mud I. 7–8, and 600 r.p.m. at 100° F. is recommended as the speed giving the least error in the measurements.

With this instrument Ambrose and Loomis [29] found a viscosity minimum at the *p*H of maximum stability—11·4—for bentonite suspensions, and also showed the decrease of apparent viscosity with increased rate of revolution of the viscometer. It was again used [30] to examine the effects of a number of chemicals on drilling muds. Caustic soda, sodium oleate, Mud-it, sap-brown, Stabilite, humic acid, tannic acid, sodium tannate, sulphite waste liquor, soda-black liquor, spent liquor, chestnut extract, and mixtures of these with varying amounts of caustic soda were used. It was found that organic materials were much superior to inorganic reagents for lowering the viscosity of muds, and the degree of gelling appeared to be almost entirely dependent on the amount of caustic soda used.

Craft and Exner [31] have used the Stormer viscometer to examine the effect of temperature (40–200° F.) on the viscosity of muds. They find that with dense muds or muds high in colloidal matter the viscosity decreases with rise in temperature up to about 140° F., and then increases with increase in temperature above that point. However, they do not indicate what precautions were taken against evaporation losses; whether the sample was kept in the viscometer throughout the range of temperatures; whether the concentration was checked after the final measurement or a repeat measurement was made at the starting temperature.

A Kämpf viscometer was used by McMillen [32] to measure the thixotropy—

isothermal sol-gel transformation—of suspensions including clays. He proposes to represent his data by :—

$$(\phi - b)(t + a)^k = K$$

ϕ being the fluidity and t the time of observation. $\phi_{t=\infty}$ increases as the shearing stress increases, and k tends to decrease with increase in shearing stress, becoming zero when the stress is sufficient to destroy all structure. McMillen points out that any time from a few minutes to several hours may be necessary, according to the shearing stress, for the attainment of thixotropic equilibrium. Hence rotational viscometers, where there is no possibility of previously undisturbed material entering the zone of shear, are better adapted for studying thixotropy.

According to Hall [9] clay slips behave plastically in a MacMichael viscometer and other difficulties arise. Nevertheless, Cunningham [33] has examined the behaviour of clay suspensions in such an instrument within a pressure chamber. Equilibrium was reached in 10 minutes at 40 lb./in.^{2} but after only 45 minutes at 2½ lb./in.^{2} The mobility increased with pressure, and due to the immediate reversal of the friction effect on removal of the pressure, a still higher mobility could be observed.

Ambrose and Loomis [34] have examined a bentonite suspension in a Hatschek type of viscometer. On a curve where torque is plotted against rate of revolution, they find that when measurements are made at successively higher speeds, and then at speeds which are decreased in steps, the former curve lies above the latter. The torque may increase or decrease with time for a constant rate of revolution, and may even require several hours to reach a constant value.

Richardson has adapted the hot-wire anemometer for measuring the velocity distribution in fluids undergoing shear in a tube or in a concentric cylinder apparatus [35, 36] He has applied it in the latter instrument to the study of clay suspensions.[37] Assuming no slip at the inner cylinder, his results confirm the hypothesis of a diminishing rigid annulus, and are characteristic of Scott Blair and Crowther's stage III. He has also measured the critical shearing stresses of the same suspensions.

Assuming the Bingham hypothesis, Reiner [38] has derived an equation for the behaviour of plastic materials in a concentric cylinder viscometer. This equation is analogous to that obtained by Buckingham for the capillary viscometer, but with the slip term omitted. He shows that if R_1 be the radius of the inner cylinder, R_2 the radius of the outer cylinder, l the wetted height of the inner cylinder, M the moment due to external forces, and f the Bingham yield value, the maximum shearing stress is at the inner cylinder, and flow commences there when $M \geqslant 2\pi R_1^2 l f$; the minimum shearing stress is at the outer cylinder and flow commences there when $M \geqslant 2\pi R_2^2 l f$. At this stage, *all the material flows*, and therein is the essential difference between plastic flow in the rotating cylinder and capillary viscometers. In the latter, this theory demands a "solid cylinder" near the axis, no matter how great the velocity, if streamline. When all the material is in flow the outer cylinder has an angular velocity given by :—

$$\Omega = \mu \frac{M}{4\pi l}\left(\frac{1}{R_1^2} - \frac{1}{R_2^2}\right) - \mu f \log_e \frac{R_2}{R_1},$$

which is a linear relationship between Ω and M.

Falling and Rolling Sphere Viscometers.

Strong [23] finds that " for studies of muds near the limit of pumpability . . . the rate of descent of metal spheres appears to be more convenient " (than the use of his modified funnel viscometer). The Höppler [39] viscometer is said to be applicable to opaque liquids, and may therefore be suitable for muds, and there seems no reason why the rolling sphere viscometer of Flowers [40] should not be adapted for the same purpose.

It would appear that none of the existing viscometers is entirely satisfactory for measuring the fluid constants of these clay suspensions. For samples prepared in the laboratory the time and method of preparation affect the results. The presence of thixotropy raises difficulties in measurements with capillary or other instruments which do not normally permit the attainment of thixotropic equilibrium. On the other hand, it would appear that the comparatively long time necessary for attaining that equilibrium in the concentric cylinder apparatus, would render the fair definition of the flow curve a lengthy task, and thereby permit the entry of other factors, such as sedimentation, in all but the most ideal suspensions. Hence it will be clear that it is necessary to keep the method of measurement in mind in considering the following results.

The viscometer used consisted of a glass bulb holding a little more than 40 c.c.s. between the etched marks, with a capillary held in position at the bottom of the bulb by means of a piece of pressure tubing. The outer glass container was a 10-in. gas jar, the capillary being kept along the axis of the jar by four radial wire guides attached to the piece of pressure tubing. The whole was placed in a water-bath, the temperature of which could be maintained constant to within less than one-tenth of a degree Centigrade.

A suitable quantity of the mud was poured into the gas jar and brought to the required temperature in the bath. The viscometer was placed in its special holder with the capillary immersed in the mud, and suction was applied to bring the mud to the lower graduation inside the bulb, the tap A at the top then being closed. The mud level in the jar was now adjusted to the lower graduation on the bulb by adding mud from a bottle, also in the bath, which contained a further quantity of the mud. Meanwhile the air pressure in a reservoir had been reduced to a suitable value, and maintained thus by a screw clip on the pressure tubing, which was attached to the viscometer at this stage. The actual measurement consisted of opening the screw clip, observing the manometer reading, opening tap A, and measuring the time to fill to the upper mark on the bulb. The manometer was again read, tap A having been closed as soon as the mud had passed the upper mark. After removing the viscometer, the mud it contained was returned to the jar to regain the bath temperature (as a rule the time of flow was short and the temperature difference between the atmosphere and the bath small, so that its temperature could have changed but little), and mud was added from the bottle to replace working losses. The viscometer was then washed and dried ready for a second measurement.

The instrument was calibrated by means of sucrose solutions and water, and an instrumental correction was calculated which was considered to allow for conicality or other irregularities of the capillaries, and for imperfect

end and hydrostatic head corrections in the case of true fluids. The suspensions were made up in distilled water, and it was necessary to force the Aquagel through a screen in order to break down clots.

The results have been expressed in two ways. In one, the "viscosity" has been calculated as that of a hypothetical normal fluid which under the same pressure gradient would have the same time of flow, this value being plotted against the mean average velocity (since there is a hydrostatic head correction the rate of flow falls off as a single measurement proceeds). The ordinary equation was used, the value of P being that corrected for hydrostatic head and also the instrumental correction.

$$\eta = \frac{\pi P R^4}{8V(L + nR)} - \frac{mV\rho}{8\pi(L + nR)}$$

The hydrostatic head correction applied is only approximate, for the shape of the bulb renders an exact computation exceedingly complex [41]

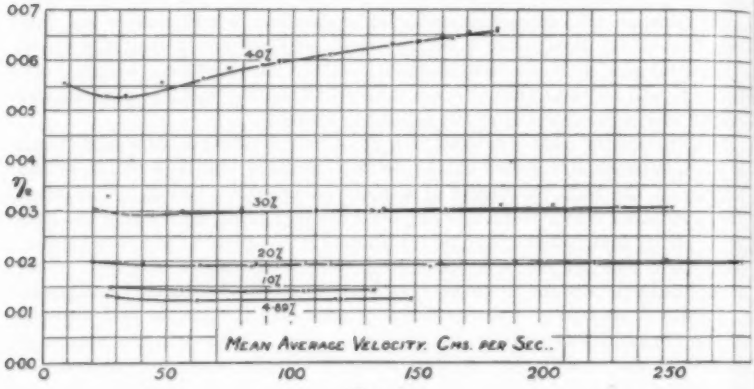

Fig. 1.

STOCKOLITE SUSPENSIONS AT 15° C. RADIUS OF CAPILLARY—0·0434 CM.

even for true fluids, and the fact that anomalous systems are under consideration introduces further difficulties. The "viscosity" calculations being made for a hypothetical true fluid, it would appear quite legitimate to use those constants applicable to a true fluid.

In the second method $\frac{V}{\pi R^3}$ was plotted against $\frac{PR}{2L}$.

The equivalent viscosities have been given in terms of poises, not because the results are in any way absolute, but to give a clearer idea of the magnitudes of the "viscosities," whilst the dimensions of $\frac{V}{\pi R^3}$ and $\frac{PR}{2L}$ are respectively secs.$^{-1}$ and dynes/sq. cm.

Figs. 1 and 2 show the results of measurements on a series of stockolite suspensions. The equivalent viscosity is seen to be dependent on the velocity of flow. The curves of Fig. 2 all seem to pass through the origin when produced, which would indicate that there is no yield value, and hence

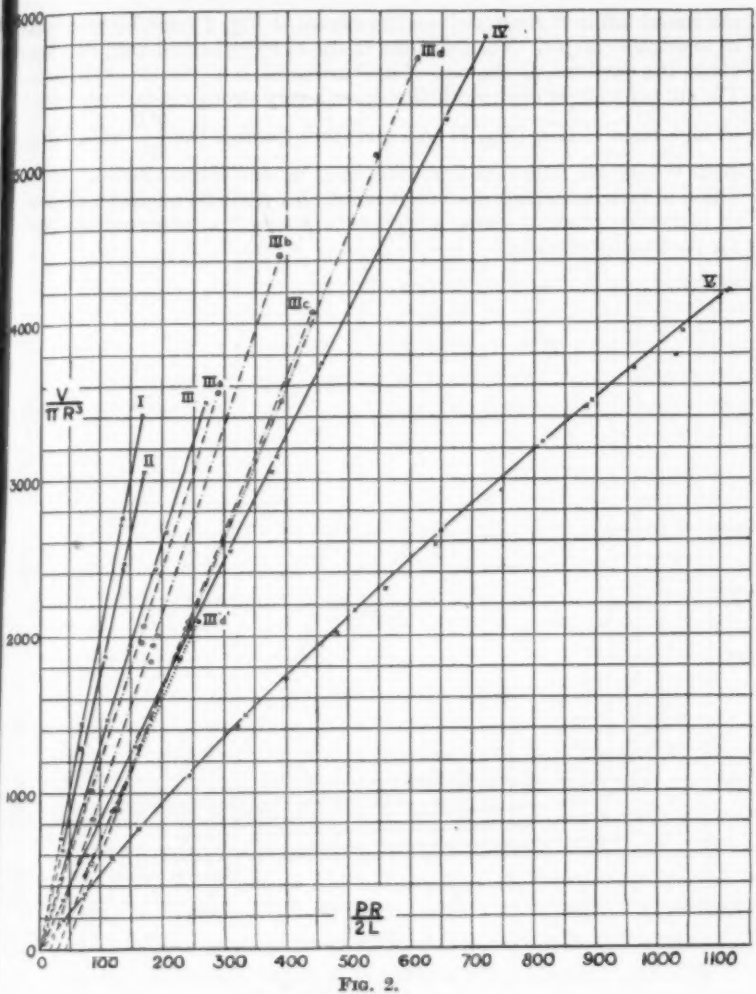

FIG. 2.

MEASUREMENTS AT 15° C.

Radius of Capillary—0·0434 cm. :—

I. 4·89% Stockolite.
II. 10·00% „
III. 20·00% „
IV. 30·00% „
V. 40·00% „
IIIa. 20% Stockolite with 0·0658% hydrochloric acid.
IIIb. „ „ „ 0·0846% „ „
IIIc. „ „ „ 0·1034% „ „
IIId. „ „ „ 4·90% caustic soda.

Radius of capillary—0·0638 cm. :—

IIId. 20% Stockolite with 4·90% caustic soda.

the initial fall in " viscosity " on the curves of Fig. 2 must be attributed to some other factor. The reduction in size of hypothetical fluid envelopes about the particles, as the rate of flow increases, is a possible explanation. The curve for 40 per cent. stockolite shows a very strong rise in " viscosity " at high rates of flow (Fig. 1) and curvature towards the $\frac{PR}{2L}$ axis. Scott Blair [17] suggests that such curvature may be due to turbulence. In addition to turbulence, it is possible that complex particles might break down at high rates of shear giving a higher " viscosity," as observed by Oden, for the smaller particles.

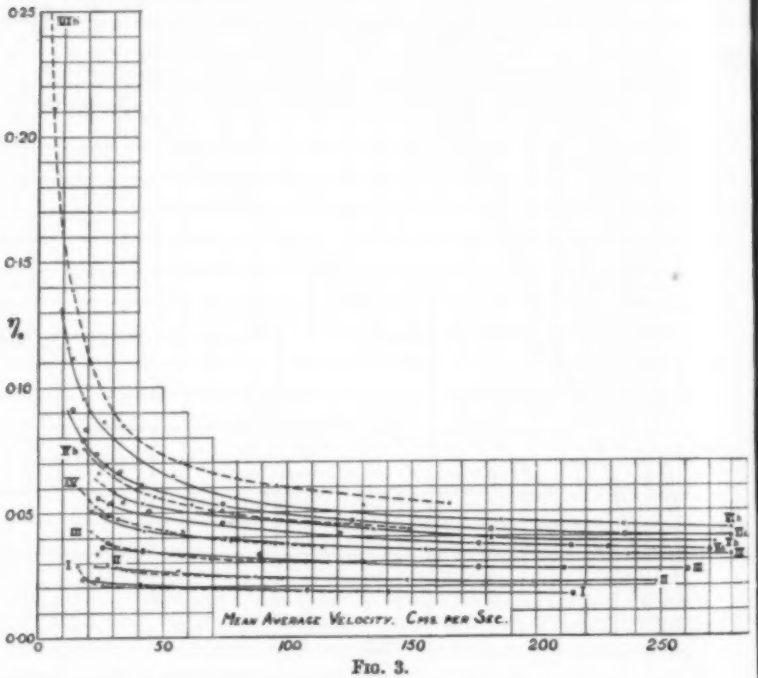

FIG. 3.

The data obtained for a number of Aquagel suspensions are shown in Figs. 3 and 4. The equivalent viscosity falls off very quickly as the mean average velocity increases, and the flow curves (Fig. 4) are almost straight at low concentrations, but become curved as the concentration increases, particularly at low " rates of shear."

Attempts to find relationships between the concentration and the " viscosity " of these suspensions encounter the initial difficulty that the " viscosity " is dependent on the rate of flow. Presumably the limiting " viscosity " or the mobility^{-1}, derived from the flow curves, should be used, but even for the latter quantity a reasonable value does not seem to be obtainable in all cases. Using the concentration by weight, the relation-

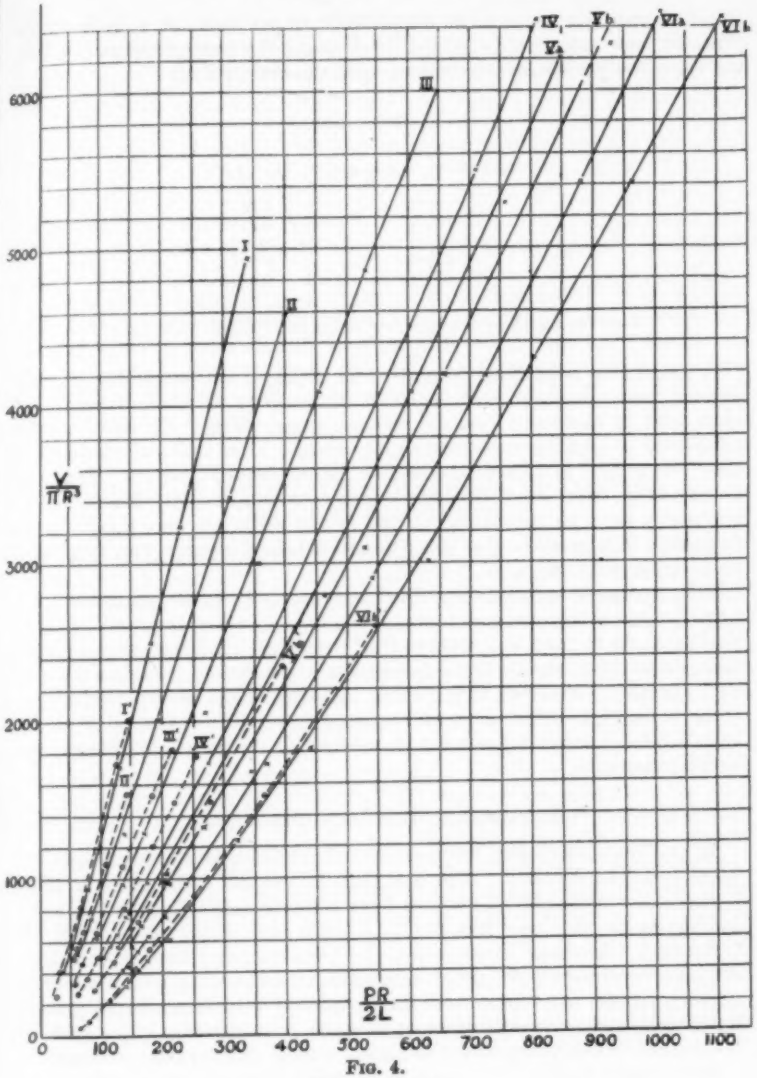

FIG. 4.

FIGS. 3 and 4.

AQUAGEL AT 15° C.

Radius of capillary—0·434 cm. :— ————————
—0·0638 cm. :— - - - - - - - -

I.	0·989%	Aquagel.	Va.	4·252%	Aquagel.
II.	1·984%	,,	Vb.	4·697%	,,
III.	2·925%	,,	VIa.	5·188%	,,
IV.	3·820%	,,	VIb.	5·586%	,,

ship for stockolite seems to be linear up to 10 per cent., or even to 20 per cent. for some rates of flow, whilst for Aquagel the concentration at which the curve steepens seems to increase with the rate of flow.

TABLE 2.

Concentration of Aquagel.	Mobility^{-1}.
0·989%	0·0177
1·984%	0·0210
2·925%	0·0256
3·820%	0·0312
4·697%	0·0373

Data for capillary of radius 0·0638 cm., and length 11·644 cm.

A suspension containing a mixture of Aquagel and stockolite was examined, and compared with separate suspensions in which the ratio of each solid to the water present, was the same. The " viscosity " of the composite suspension was considerably greater than that calculated from the " viscosity " increments caused by the separate materials. This may be expected, since the " viscosity " increases more rapidly than the concentration for a single substance, and as the materials were mixed in the dry state, it is possible that the Aquagel attained greater dispersion than in a simple suspension.

This composite suspension formed a strong jelly on standing for a few days, but could be converted to a uniform fluid by a few moments' vigorous shaking. At the age of 9 months its " viscosity " had increased by more than 40 per cent., and if stirred during a measurement, it showed a decrease in " viscosity " of about 10 per cent. Stirring might be expected to promote turbulence and so give an apparent increase in " viscosity," but if turbulence did arise, it was more than offset by the increase in fluidity due to the stirring.

TREATMENT WITH ACID AND ALKALI.

20 per cent. stockolite suspensions were treated with caustic soda and with hydrochloric acid. The addition of caustic soda gives a slight " viscosity " minimum at about 0·4 per cent. of soda (expressed as a percentage of the dry clay present) for a given rate of flow, after which the " viscosity " increases slowly, up to 2·5 per cent., and then more quickly at higher concentrations. For treatment with acid there is a faint minimum at about 0·035 per cent.; and the " viscosity " increases rapidly above 0·065 per cent. In both cases at a given concentration of reagent the " viscosity " of the suspension increased a little on standing overnight.

When these reagents are added to the stockolite suspensions, the equivalent viscosity–mean average velocity curves change in form as the concentration of the reagent increases. The equivalent viscosity falls off more quickly at low rates of flow, as with Aquagel. Fig. 2 gives the flow curves for some of the chemically treated suspensions, and the effect of the chemicals is to make the curves give intercepts on the stress axis, and at the same time decrease their slope, *i.e.* the mobility.

TABLE 3.

Material.	Intercept.	Mobility.
20% stockolite with 0·103% HCl .	42	41·3
" " 0·0846% " .	19	47·9
" " 0·0658% " .	0	48·7
" .	0	52·1
" with 1·998% NaOH	5	44·7
" " 4·900% " .	25	38·6

The data of Table 3 differ from those of Wilson and Hall.[19]

An Aquagel suspension was treated with caustic soda. It showed a continuous, but not a uniform, decrease in " viscosity " with increase in concentration of soda. Small irregularities were frequently found to coincide with the intervals when the material stood overnight before the next addition of soda. Concentrations were used up to 25 per cent. by weight of the dry Aquagel.

EFFECT OF ENTRAINED AIR ON CHEMICALLY TREATED STOCKOLITE SUSPENSIONS.

In using the untreated stockolite suspensions, a tenacious sediment formed at the bottom of the gas jar in a very short time, and this could be readily redispersed only by vigorous shaking. The air taken up in this shaking escaped with great rapidity, and did not affect the results. When these suspensions had been treated with a fair amount of soda or acid, it became evident that air bubbles were being entrained which did not escape at all quickly. Furthermore, the sedimentation which had led to the shaking method being employed was not nearly so marked in these suspensions, and could be eliminated by less vigorous methods which prevented air from being entrained. A series of measurements was made to find the effect on the " viscosity " of this entrained air. Observations were made when the suspensions were stirred between each measurement, and for 90 minutes before the first measurement, by three propellors on the same shaft, totally immersed to prevent splashing. In the second set of observations the suspensions were very vigorously shaken immediately before each measurement to incorporate the maximum amount of air.

TABLE 4.

Material.	Ratio : $\frac{\text{Equivalent viscosity air-charged.}}{\text{Equivalent viscosity air-free.}}$	
20% stockolite with :—	Mean average velocity. 20 cm./sec.	Mean average velocity. 180 cm./sec.
0·039% NaOH . . .	0·97	1·00
1·998% " . . .	0·88	0·93
6·000% " . . .	0·83	0·95
0·1128% HCl . . .	0·79	0·95

The volumetric effect alone of the air may be expected to give a low viscosity value. Table 4 shows that the effect of the air is less at high rates of flow. At these high rates of flow the pressure above the liquid in the bulb is less than at low rates of flow, and therefore the bubbles will expand more and tend to rise more quickly. On the other hand, the time during which this escape can occur will be least at the highest rates of flow. It appears that the former factor outweighs the latter. Measurements to estimate the amount of air likely to be present at the beginning of an observation, give a figure far below that necessary to account volumetrically for the whole of the apparent fall in "viscosity" due to the presence of air. Hence it seems that the air has some additional "viscosity" reducing effect.

Effect of Temperature on the "Viscosity" of the Suspensions.

Three suspensions were examined at 10° C., 20° C., and 30° C. The changes in "viscosity" at a given rate of flow for 10 per cent. and 40 per cent. stockolite over the range 10–30° C. tend to be respectively slightly less and slightly greater than for water over that range, whilst for 20 per cent. stockolite with 1·998 per cent. caustic soda, the change was decidedly less. From the flow curves for this last suspension the change in mobility is seen to differ slightly from that for water (Table 5).

Table 5.

	Mobility^{-1}. Suspension.	Viscosity. Water.
$\eta_{30°\,C.}/\eta_{10°\,C.}$	0·825	0·770
$\eta_{30°\,C.}/\eta_{10°\,C.}$	0·649	0·610
$\eta_{30°\,C.}/\eta_{20°\,C.}$	0·789	0·793

According to Hatschek, the temperature coefficient of dispersoid sols is merely that of the dispersion medium. For emulsoid sols it is always markedly greater than that of the dispersion medium. Oden's sulphur sols had a viscosity decreasing somewhat less rapidly than that of water with rise in temperature.

Stability of Treated Stockolite Suspensions.

A number of test-tubes were set up containing a standard stockolite suspension, and to one set was added a graded series of portions of hydrochloric acid, to the other caustic soda solutions. To the tubes receiving only small amounts of soda or acid, water was added so that the ratio of stockolite to water was the same in each one. The depth of the top aqueous layer was observed at definite times. In the case of the acid-treated suspensions, at the lower concentrations of acid, clear liquid appeared only slowly, and merged into a zone of steadily increasing turbidity downwards. After a few days it became evident that a compact sediment was building upwards from the bottom of the tubes. At the higher con-

centrations of acid really clear liquid appeared at the top with comparative rapidity, and the stockolite gradually subsided with no signs of differential sedimentation and building upwards from the bottom. The upper layer was very clearly defined. The stockolite in these tubes showed signs of rigidity, in that cracks appeared in it. The two types of settling were fairly sharply defined, and after standing for more than 3 months the volume of sediment in the tubes of low acid concentration was very much less than in the others. The change occurred at about 0·088 per cent. of acid. Much the same may be said of the tubes containing soda-treated stockolite, except that no cracks were observed in the sediment. The change from one type of separation to the other occurred at a little more than 1 per cent. of caustic soda. These figures are not in close agreement with the points at which the " viscosity " begins to increase rapidly.

Chemical Composition of Stockolite and Aquagel.

Stockolite is a high-grade china-clay, practically all of which passed 200-mesh. The analyses quoted are from the Imperial Institute's publication on china-clay (kaolin). 90 per cent. of Aquagel is said to pass 200-mesh, and the analysis is from the Aquagel pamphlet.

Table 6.

	Typical Cornish china-clays.		China-clay Theoretical.	Aquagel.
Silica	46·00%	47·26%	46·3%	58·2%
Alumina	40·18%	37·86%	39·8%	21·9%
Ferric oxide	0·45%	0·75%		3·8%
Magnesia	0·02%	0·04%		2·4%
Lime	0·05%	0·87%		5·9%
Soda	0·12%	0·36%		0·7%
Potash	0·33%	0·70%		
Loss on ignition	12·90%	12·24%	13·9%	6·0%
Sulphur trioxide				0·9%
Chloride				0·2%

The higher the ratio of silica to sesquioxides in a clay the greater the degree of swelling and dispersibility, the more viscous the suspensions, the greater the heat of wetting, adsorption of bases and basic dyes, and the base exchange [42]; the higher is the electrokinetic potential of the suspension when containing a given cation in the absence of added electrolyte [43] and the more stable the suspension.[44] Mattson considers the hydration of the clay to increase with the exchange capacity, *i.e.* with the ratio of silica to sesquioxides. For the two materials considered here, it is very clear that the one with the highest silica sesquioxide ratio gives the more viscous suspensions. Joseph [45] also emphasises the importance of this ratio as a guide to the plasticity of clays.

From the present work it is clear that the actual values obtained are a function of the capillary used, whether the data are interpreted as equivalent viscosities or as mobilities from the flow curves. These points have been noted by a number of observers. The use of flow curves, whilst instructive

in many ways, does not always render general comparisons a simple matter for a range of concentrations of a material, even for a single capillary. At the higher concentrations the drawing of asymptotes to the curves, to obtain the mobility, may present some difficulties, even if the suggestion of Keen [18] is followed, that no point the stress co-ordinate of which is less than twice the static rigidity should be used in drawing the asymptote. At the highest rates of flow used, under which conditions inaccuracies in the hydrostatic head corrections would probably be least, some of the curves still do not approach linearity, and deviations are in opposite directions for the two materials examined. Hence it has been necessary to make comparisons, in many instances, in quite an empirical manner.

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